

APPENDIX D

BNL –THERMAL ANALYSIS OF PAD A SALT USING DIFFERENTIAL SCANNING CALORIMETRY

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September 8, 1999

Peter Shaw
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Dear Peter

Enclosed please find the final report on the Thermal Analysis of Pad A Salt. If you need further clarification or information, please do not hesitate to call.

Regards,

A handwritten signature in black ink, appearing to read "JH Heiser".

John H. Heiser
Environmental & Waste Management Group

Enclosure
JHH/aks99L01

Cc: G. Beitel

Thermal Analysis of INEEL Pad A Salt Waste using Differential Scanning Calorimetry

Prepared by
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Differential Scanning Calorimetry (DSC) is a thermal analytical technique used to characterize specific heat and enthalpies of transition, of a sample relative to a reference material. In DSC, the sample and reference substances are heated in separate holders. Temperatures of the two materials are controlled by average temperature circuits to match a pre-determined temperature ramp (programmed time-temperature). A differential temperature circuit measures the small differences between the sample and reference holders and proportions the power to each holder to keep the temperatures equivalent. The difference in power is proportional to the heat absorbed or evolved by the sample (e.g., during transition such as melting or crystal phase changes, during endothermic or exothermic reactions).

The Environmental & Waste Management Group (EWMG) at Brookhaven National Laboratory (BNL) used DSC to analyze Pad A salt (RFP Series 745 Sludge) and assess interactions between the Pad A waste and Texaco Regal Oil 32. The salt waste originally came from Rocky Flats Plant (RFP) and was buried at the Idaho National Engineering and Environmental Laboratory (INEEL). Pad A waste contains a mix of sodium nitrate (53.9%), potassium nitrate (33.9%), sodium chloride (3.2%), potassium chloride (2.2%), sodium sulfate (2.8%), potassium sulfate (1.8%), sodium phosphate (0.9%), potassium phosphate (0.6%), sodium fluoride (0.4%) and potassium fluoride (0.3%). The salt also has trace amounts of radioactive and hazardous constituents, including approximately 185 pCi/g Uranium, 0.3 pCi/g Pu-239, 0.3 pCi/g Am-241, 0.1 pCi/g Cs-137, and 74 pCi/g K-40. The salt waste used in the study was actual Pad A waste and was supplied by INEEL. Figure 1 depicts the salt as received. The oil used was a surrogate of an oil that was co-disposed with the salt in shallow land burial pits at the INEEL. The surrogate oil was Texaco Regal Oil 32 and was selected and supplied by INEEL.

Testing was performed in accordance to ASTM method E-537, "Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis." [1] DSC runs were performed for the Pad A salt and the Texaco Regal Oil 32 separately and for a mix of Pad A salt plus a stoichiometric amount of the Texaco Regal Oil 32 (87 wt-% salt and 13 wt-% oil) and Pad A salt plus 70% of the stoichiometric amount of the Texaco Regal Oil 32 (91 wt-% salt and 9 wt-% oil). The analyses were performed to determine if any adverse reaction(s) occurred between the salt and oil.

Between 40 and 60 mg of each material or mix was loaded into individual 6 mm diameter aluminum pans which were subsequently sealed with aluminum covers. The cells used were capable of withstanding 50 atmospheres of pressure (see Figure 1). Replicate samples of each material were prepared and tested using a Shimadzu DSC-50 (see Figure 2). Test runs were

performed from ~25 °C to 400 °C at a heating rate of 2 °C/min. The furnace atmosphere was nitrogen gas flowing at approximately 20 cc/min. The reference material for each run was an identically prepared empty aluminum cell. Results of running the salt alone showed exothermic reactions between the high-pressure aluminum pan and salt occurring between 300 °C and 400 °C (see Figure 3).

The materials were then re-run using gold pans. These pans, while crimp-sealed, were capable of withstanding normal atmospheric pressure only. Runs were performed at 10 °C/min to increase the mW/mg-min and gain better sensitivity on the fine details.

The results (Figure 4) for the Pad A salt waste alone showed a clean thermogram with only endothermic peaks. Peaks occur at the as expected locations. There are two peaks below 100 °C that correspond to the loss of water of hydration for sodium sulfate [10 H₂O and 7 H₂O]. Following this is the transition peak for potassium nitrate [129 °C] and the composite melting point peaks for sodium and potassium nitrates. These melting points are depressed to 200 °C to 260 °C as opposed to referenced melting points for the individual salts of 307 °C and 334 °C for sodium nitrate and potassium nitrate, respectively. These thermogram characteristics are similar to thermograms of RFP salt waste tested at BNL in the late 1980s.[2]

The thermogram for the Texaco Regal Oil 32 is depicted in Figure 5. The oil shows a broad evaporation endothermic peak centered around 300 °C. The broad nature of the peak is as expected for an oil distillate. The oil was completely evaporated away by 350 °C. The oil run in a 50 atmosphere sealed aluminum pan is presented in Figure 6 for comparison.

The stoichiometric mix of salt and oil (87 wt-% salt and 13 wt-% oil) termed Mix A and the second mix (91 wt-% salt and 9 wt-% oil) termed Mix B were prepared in macro amounts (~1 gram) and a sub sample of this was taken for DSC analysis. The mixes were prepared by weighing out the salt and oil into a clean and dry, glazed crucible and mixing with a Teflon spatula for 2 minutes. This was done to be certain that intimate mixing of the oil and salt occurred.

The thermograms for Mix A and Mix B are presented in Figures 7 and 8 respectively. Note the similarity to the salt alone thermogram (Figure 4). Up to 400 °C there does not appear to be any adverse reactions (exotherms, which would show up as peaks in the upward direction). The only notable differences are the first two peaks that are assigned to water loss from hydrates are shifted slightly higher in temperature. This would be expected as the oil coating the salt should slow dehydration processes. The composite melting point is in the same position in the mix as in the salt alone thermogram. Since the oil is expected to evaporate completely by 350 °C, no reaction between the salt and oil would be noted above this temperature under normal atmospheric pressures. [For ease of interpretation, a composite of the thermograms is presented in Figure 9.] There is some evidence of exothermic behavior above 400 °C. This activity is small and needs confirmation through replicate runs (See results presented later for platinum pans).

The gold pan runs were completed in only single runs for each material. BNL had a few extra gold pans available from prior studies but not enough for replicate runs. Contacting the manufacturer to obtain additional gold pans (or preferably pressure-capable, gold-plated,

Figure 9 Thermograms of INEEL Pad A Salt, Texaco Regal Oil 32, Mix A and Mix B

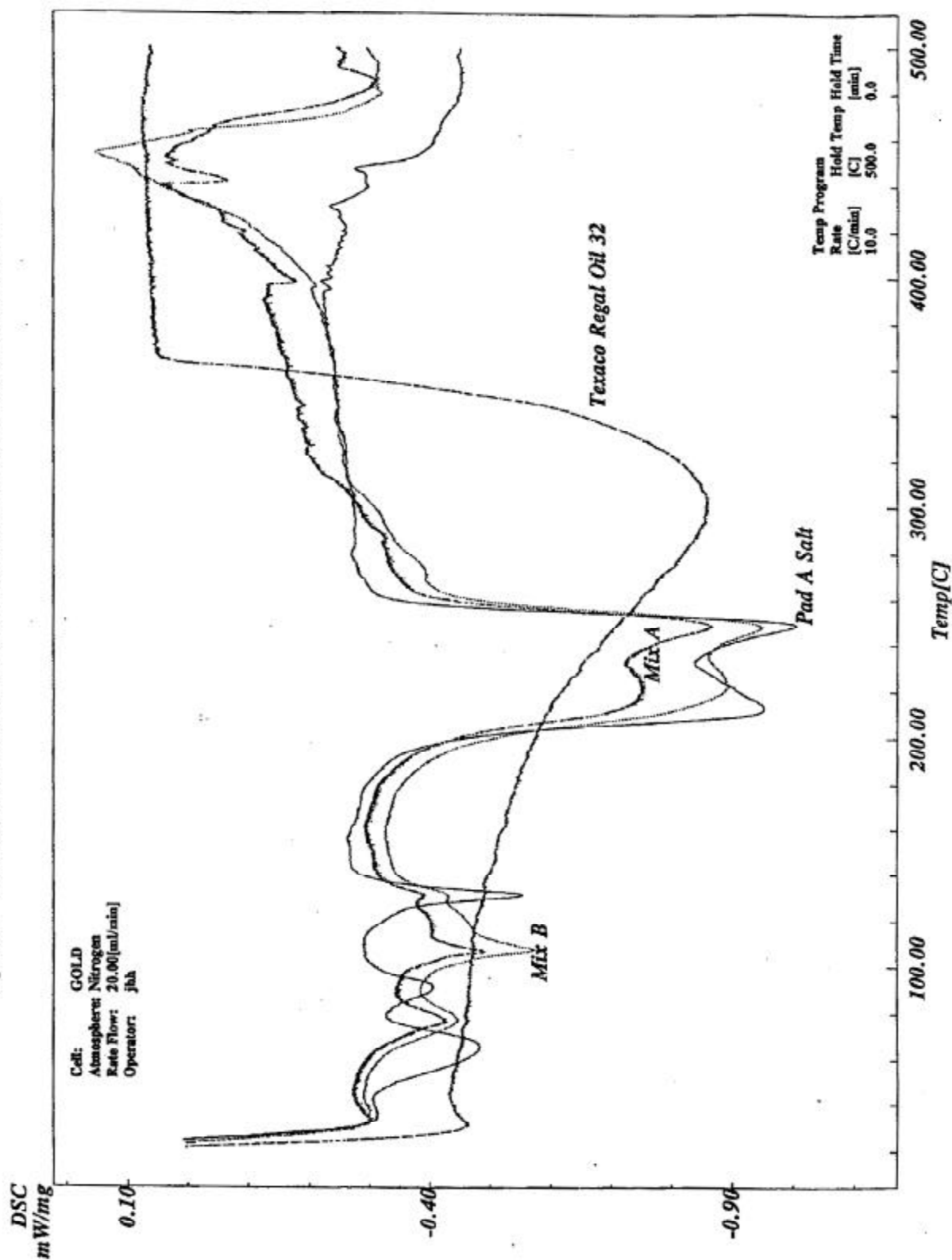


Figure 10 Thermograms of INEEL Pad A Salt Waste

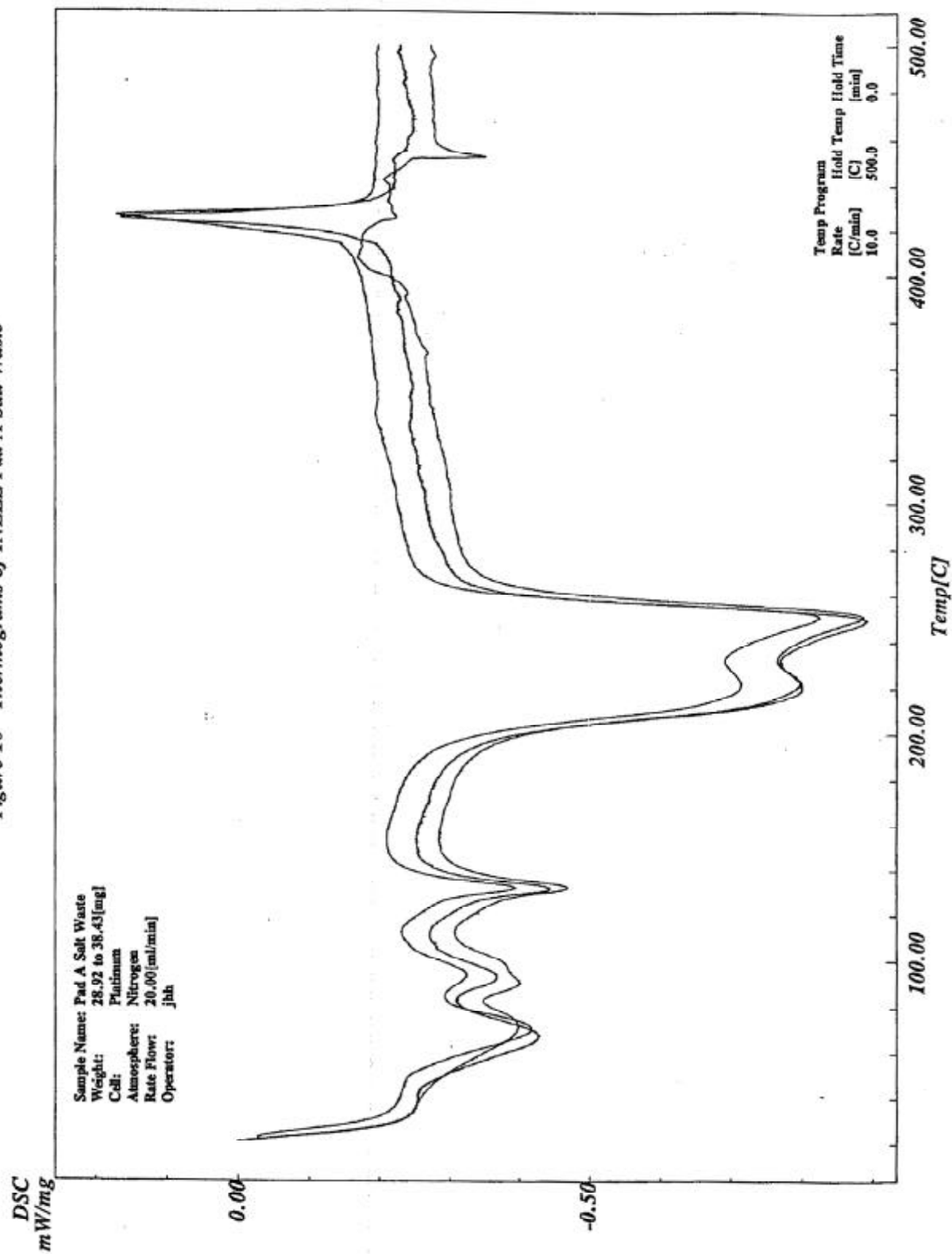


Figure 11 Thermograms of Texaco Regal Oil 32

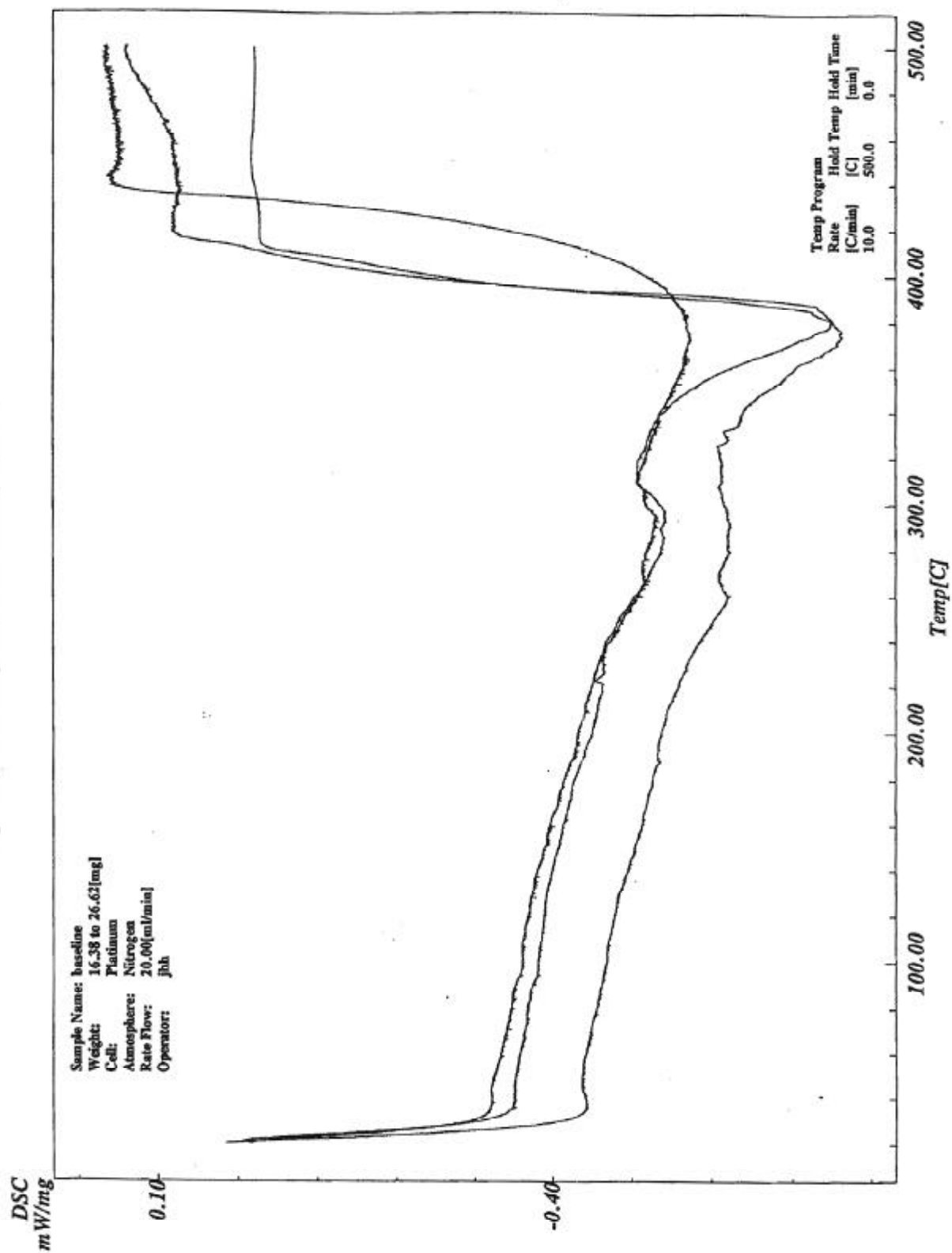
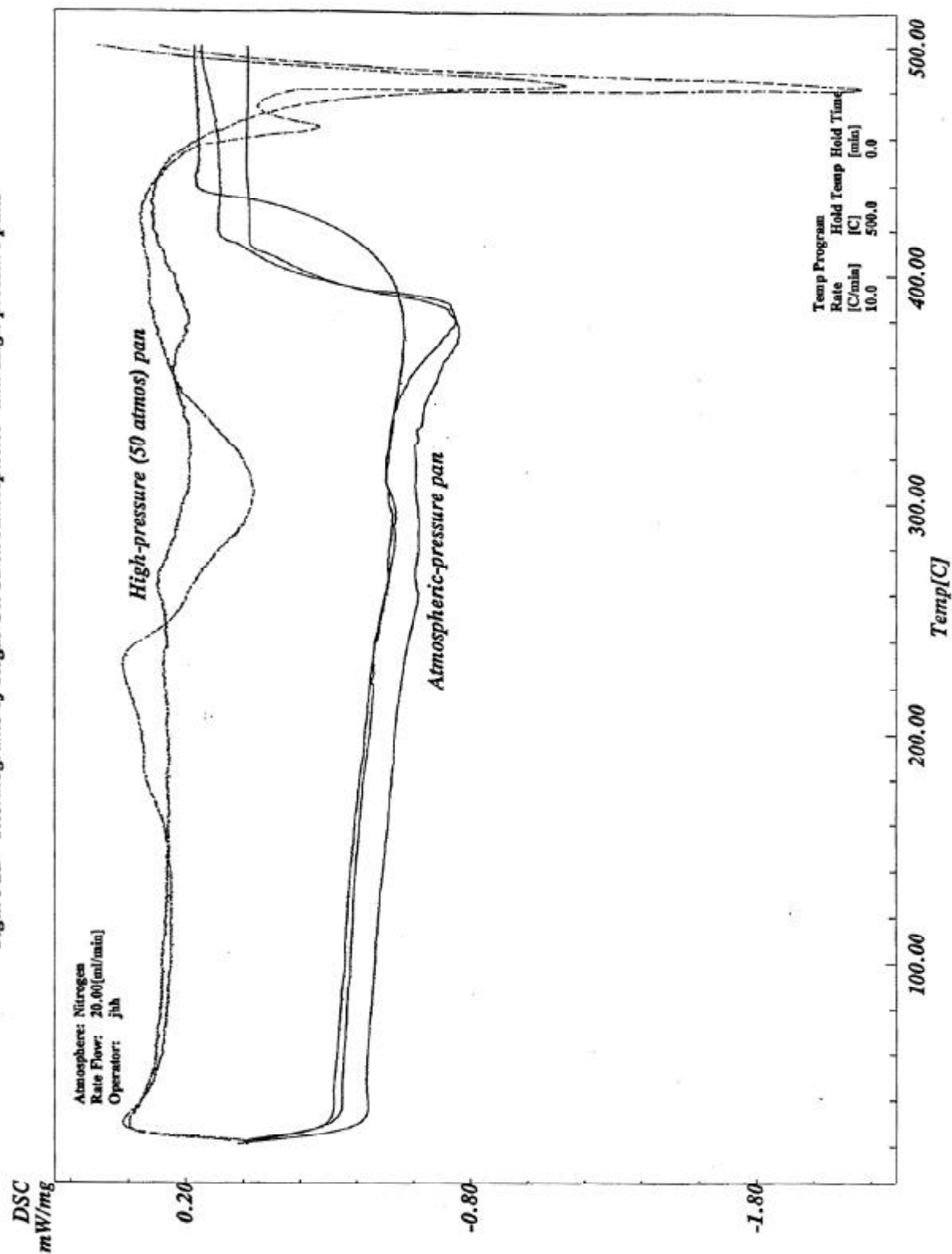


Figure 12 Thermograms of Regal Oil 32 in Atmospheric- and High-pressure pans



stainless-steel pans) was unsuccessful as the pans were out of stock and back-ordered until October 1999. INEEL's need for immediate information precluded waiting for such a long period, so with the concurrence of INEEL, BNL used platinum pans that were only capable of atmospheric pressure. Each of the materials; Pad A salt, Regal 32 Oil, Mix A and Mix B were run in triplicate in the platinum pans. The results are presented in Figures 10 - 16.

The Pad A salt thermograms (Figure 10) show a unique exotherm not previously seen. Just past 400 °C, a sharp exothermic peak occurs in two out of three runs. In the third, the thermogram is similar to that in the gold pan, a small blip occurs in this region of interest. This may imply some organic contamination within the salt and that the contamination is not uniformly dispersed. Since the salts came from an aqueous solution, the soluble inorganic components are expected to be evenly dispersed. The organic components may not have been water soluble and therefore did not get evenly dispersed.

The Texaco Regal Oil 32 Oil thermograms (Figure 11) are similar to the gold run. The oil slowly evaporates and is gone in all cases by 420 °C. For comparison, the high-pressure pan DSC results are composited with the platinum atmospheric pressure DSC runs in Figure 12.

The thermograms for Mix A (Figure 13) and Mix B (Figure 14) are similar to the salt alone with the exception that the small exotherm above 400 °C is very noisy and not a distinct singlet as seen in two out of the three salt alone graphs. Thermograms of Mix A and Mix B are composited in Figure 15. There is no difference noted between the two mixes. Figure 16 composites all the platinum DCS curves for the salt alone, the oil alone and Mix A and Mix B. Note that the minor exotherms generally occur in the region above 400 °C and after the evaporation of the oil. There does not appear to be any interaction between the salt and oil and certainly no major adverse reaction between the salt and oil occurs up to 400 °C, the original temperature requirement.

As a comparison, INEEL requested DSC runs in platinum pans for Pad A salt mixed with graphite and Pad A salt mixed with sawdust. In both cases the stoichiometric (87 wt% salt, 13 wt% fuel) ratio was used. The graphite used was a spectroscopic grade powder with less than 6 ppm total impurities. Sawdust was a hardwood dust that was sieved to provide a fine dust. Thermograms for the graphite alone and the sawdust alone are presented in Figures 17 and 18 respectively. The mix of salt and graphite are shown in Figure 19 and the composite of Pad A salt alone, graphite alone and the mix of salt and graphite is given in Figure 20. Only very minor activity is noted near 400 °C and the graphs resemble the salt alone thermograms. The sawdust alone shows a large endotherm below 100 °C attributed to water loss and a large exotherm occurring between 300 °C and 400 °C, which is attributed to decomposition/oxidation of the wood. The salt sawdust (Figure 21) shows the smaller endothermic peak near 100 °C and two large exothermic peaks beginning at ~300 °C and continuing until nearly 500 °C. This is an obvious and large interaction between the salt and sawdust. Note also that the second peak, which is not seen in the sawdust alone, is sharper than the first and is in the same position as the small distinct exothermic peaks occasionally seen for the Pad A salt alone. The interactions are more clearly seen in the composite thermogram (Figure 22) with the Pad A salt alone, Sawdust alone and the salt sawdust mix.

This large reaction and typical exothermic peak is the type one would look for to determine if any serious adverse reactions would occur between the Pad A salt and the organic oil. The lack of any major exothermic activity is good evidence that little interaction between the Pad A salt waste and Texas Regal Oil 32 will occur up to temperatures of 400 °C.

References

1. American Society for Testing and Materials, "Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis", Philadelphia, PA, ASTM E-537 (76).
2. Heiser, J.H., Franz, E., and Colombo, P., "A Process for Solidifying Sodium Nitrate Waste in Polyethylene", Fourth International Symposium on Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes, May 3-6, 1987, Pierre Cote and Michael Gilliam editors, American Society for Testing and Materials, STP 1033, (1989).

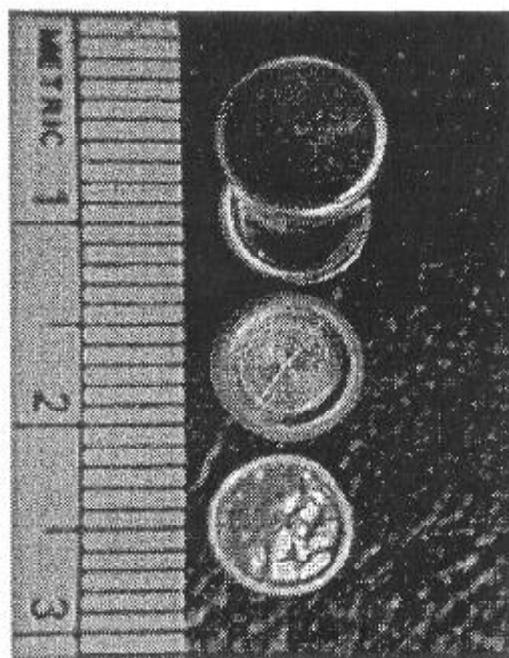


Figure 1 Differential Scanning Calorimetry sample pans (left to right, gold, high-pressure aluminum and platinum.

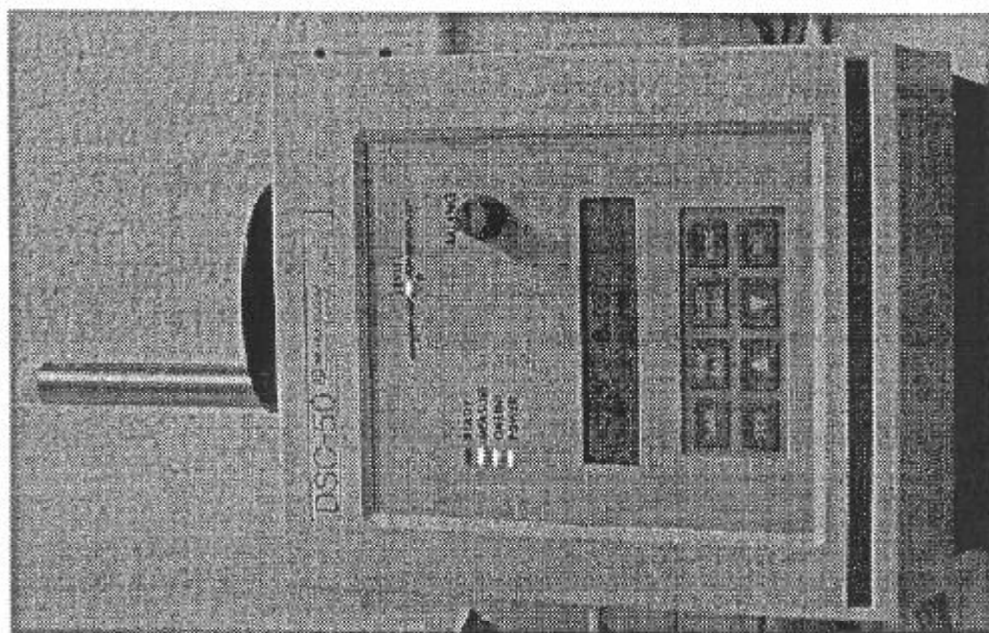


Figure 2 Shimadzu DSC-50 Differential Scanning Calorimeter.

Figure 3 Thermograms of INEEL Pad A Salt Waste in high-pressure sample pans

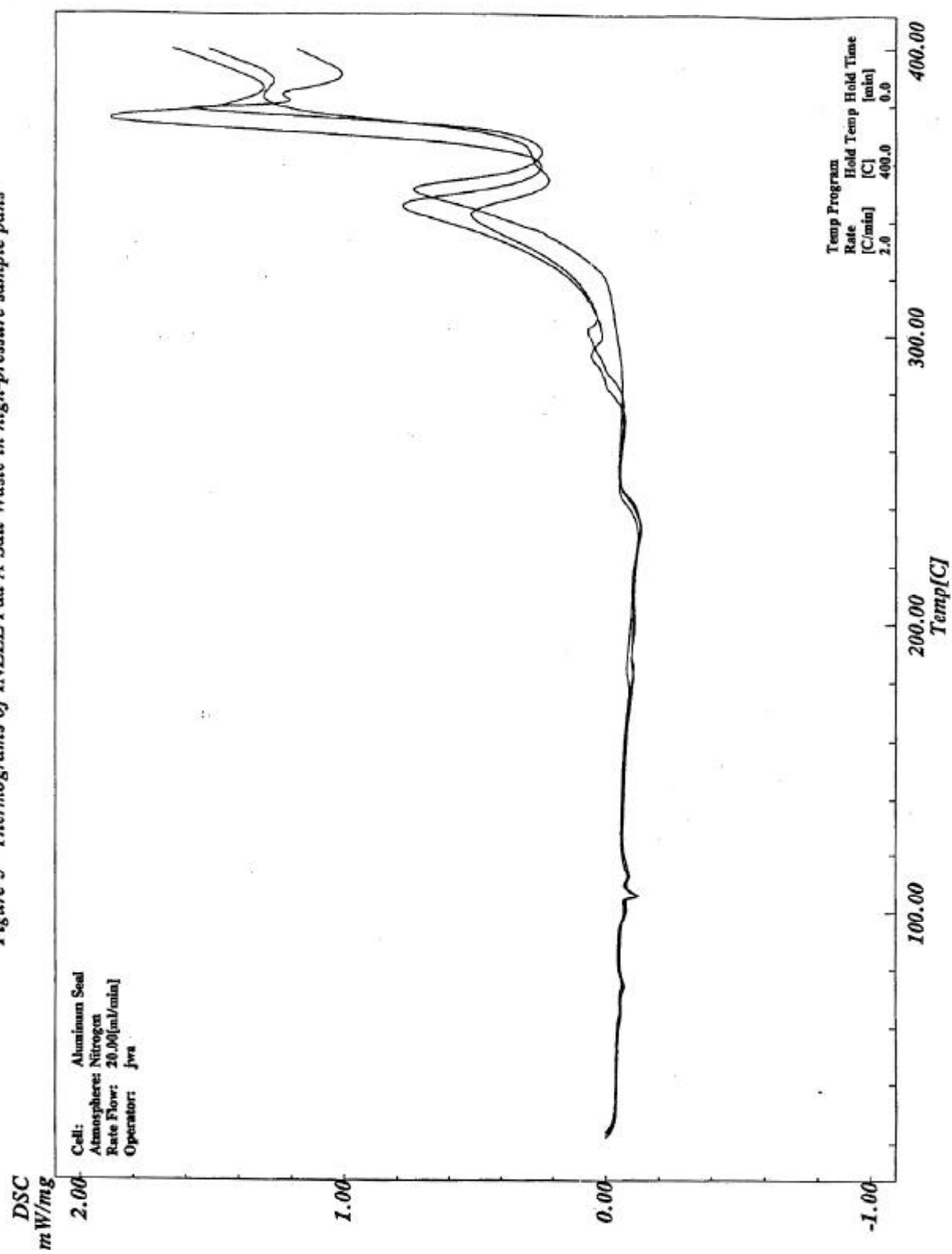


Figure 4 Thermogram of INEEL Pad A Salt Waste in gold sample pan

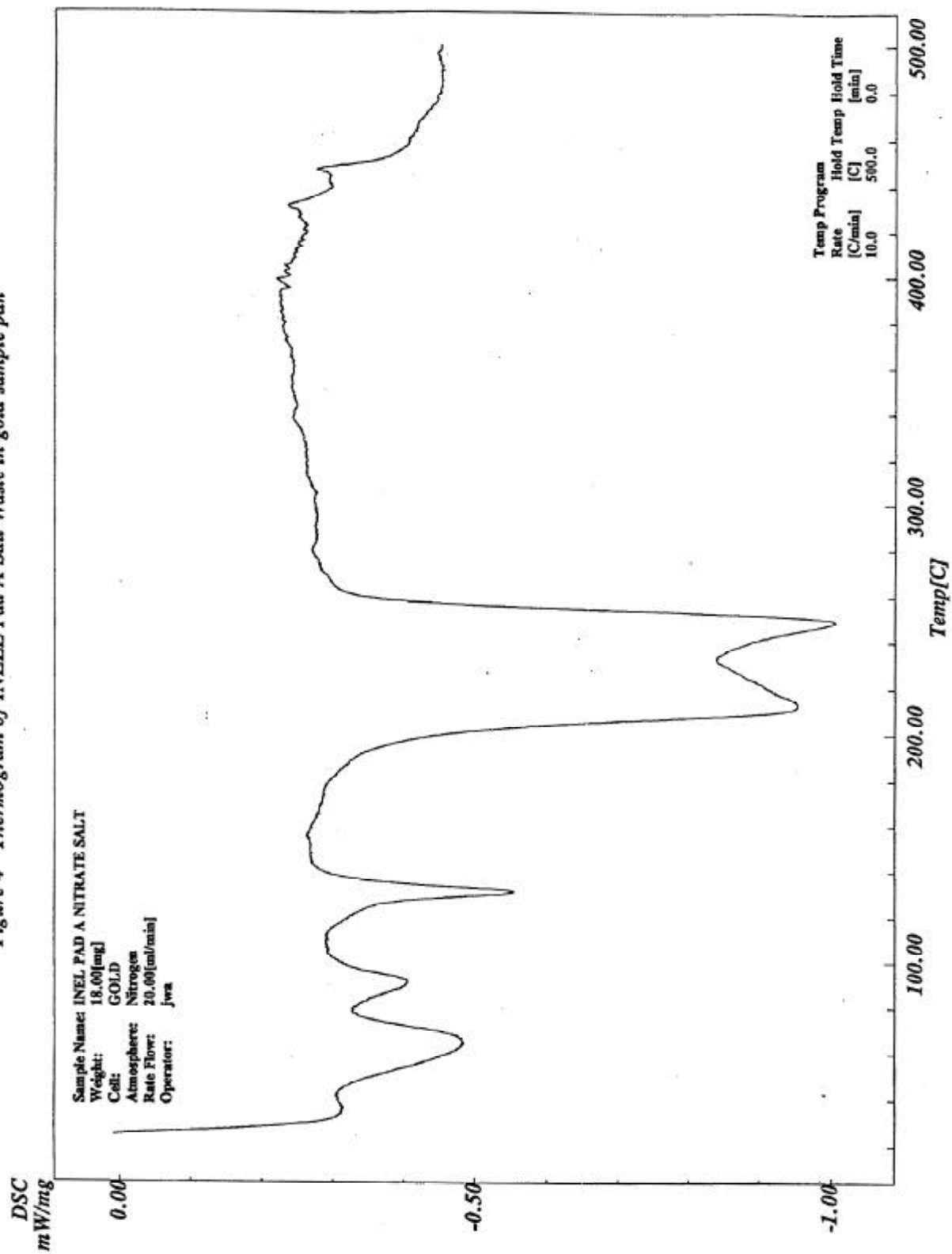


Figure 5 Thermogram of Texaco Regal Oil 32 in gold sample pan

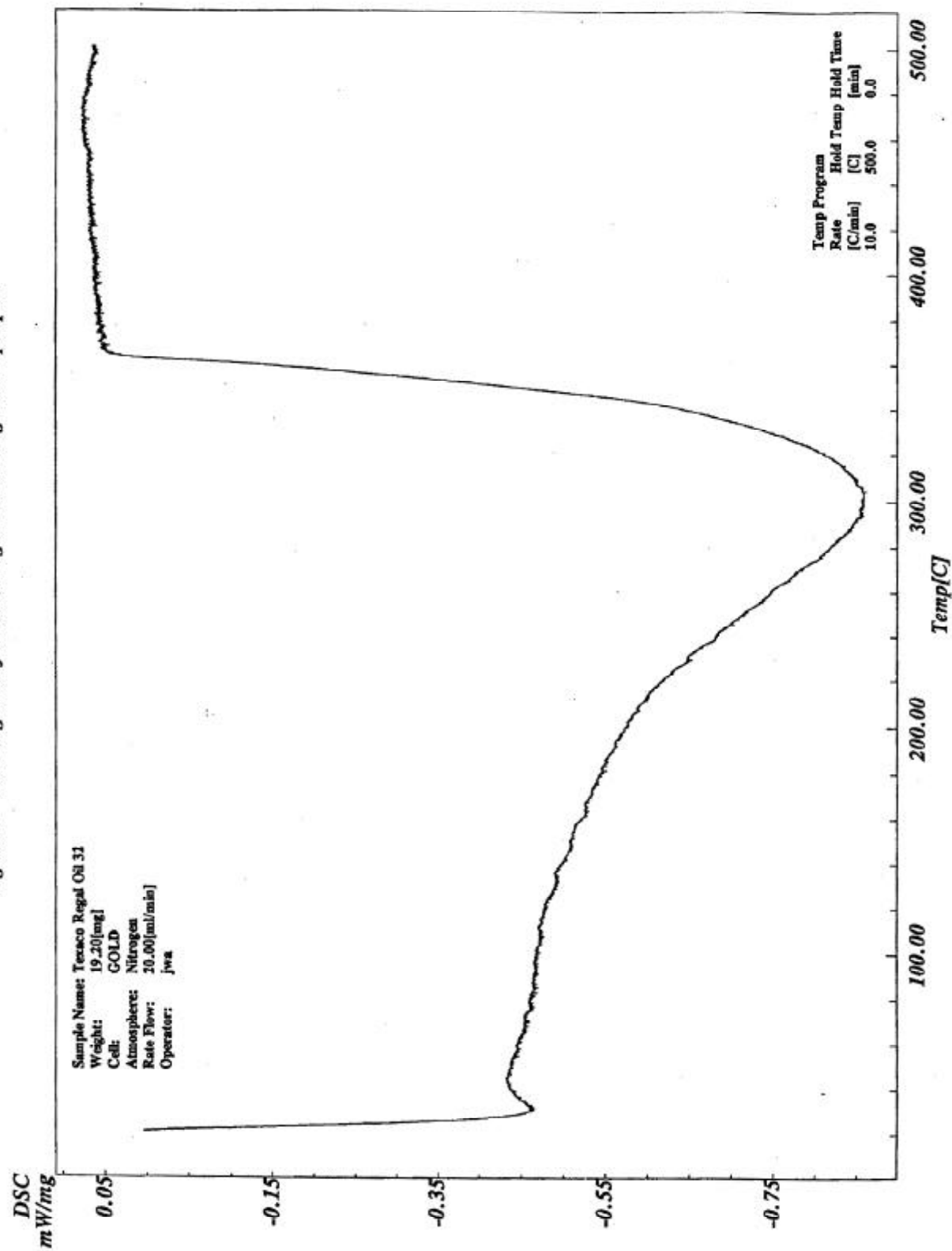


Figure 6 Thermograms of Texaco Regal Oil 32 in high-pressure sample pan

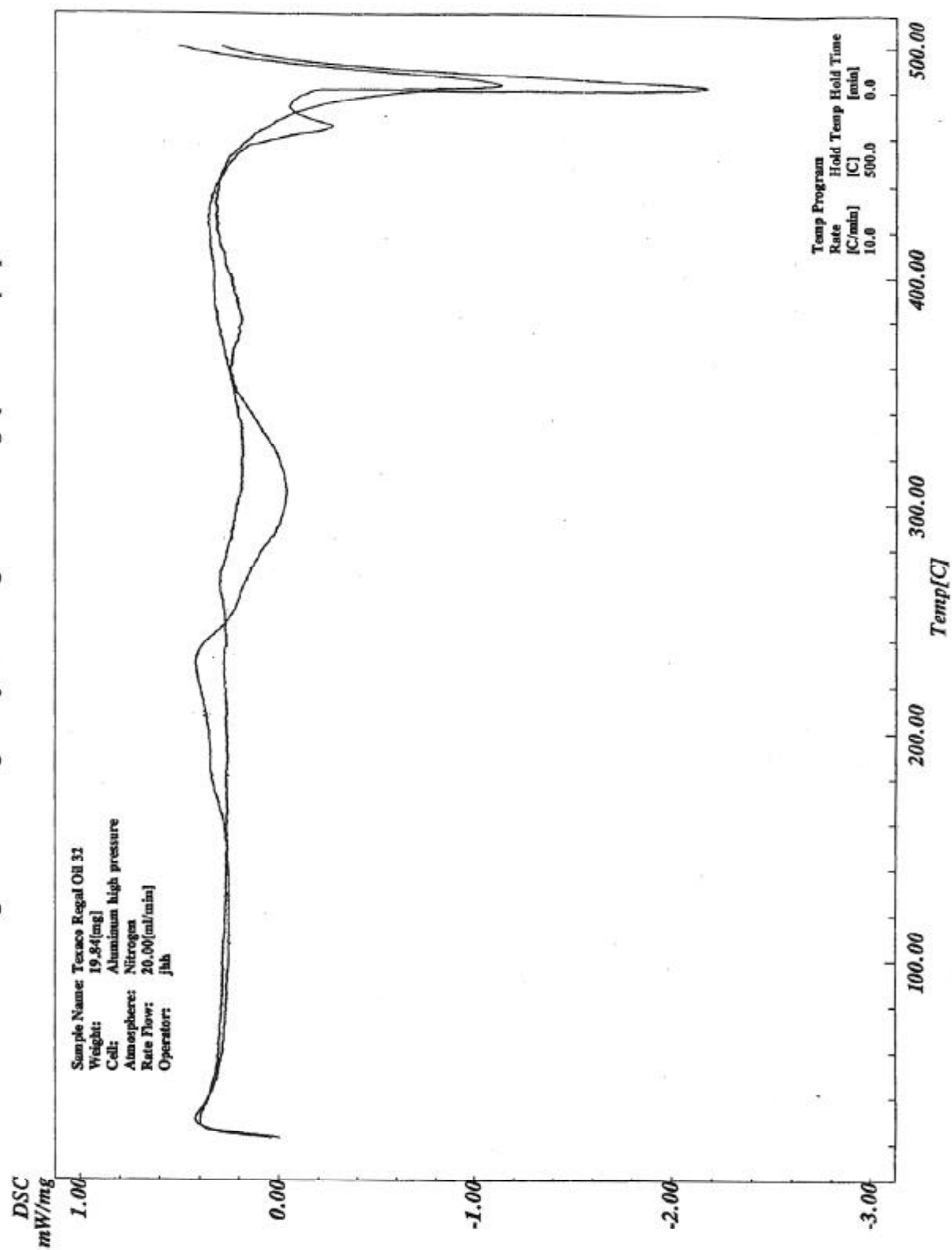


Figure 7 Thermogram of Mix A [87 wt% salt + 13 wt% oil] in gold sample pan

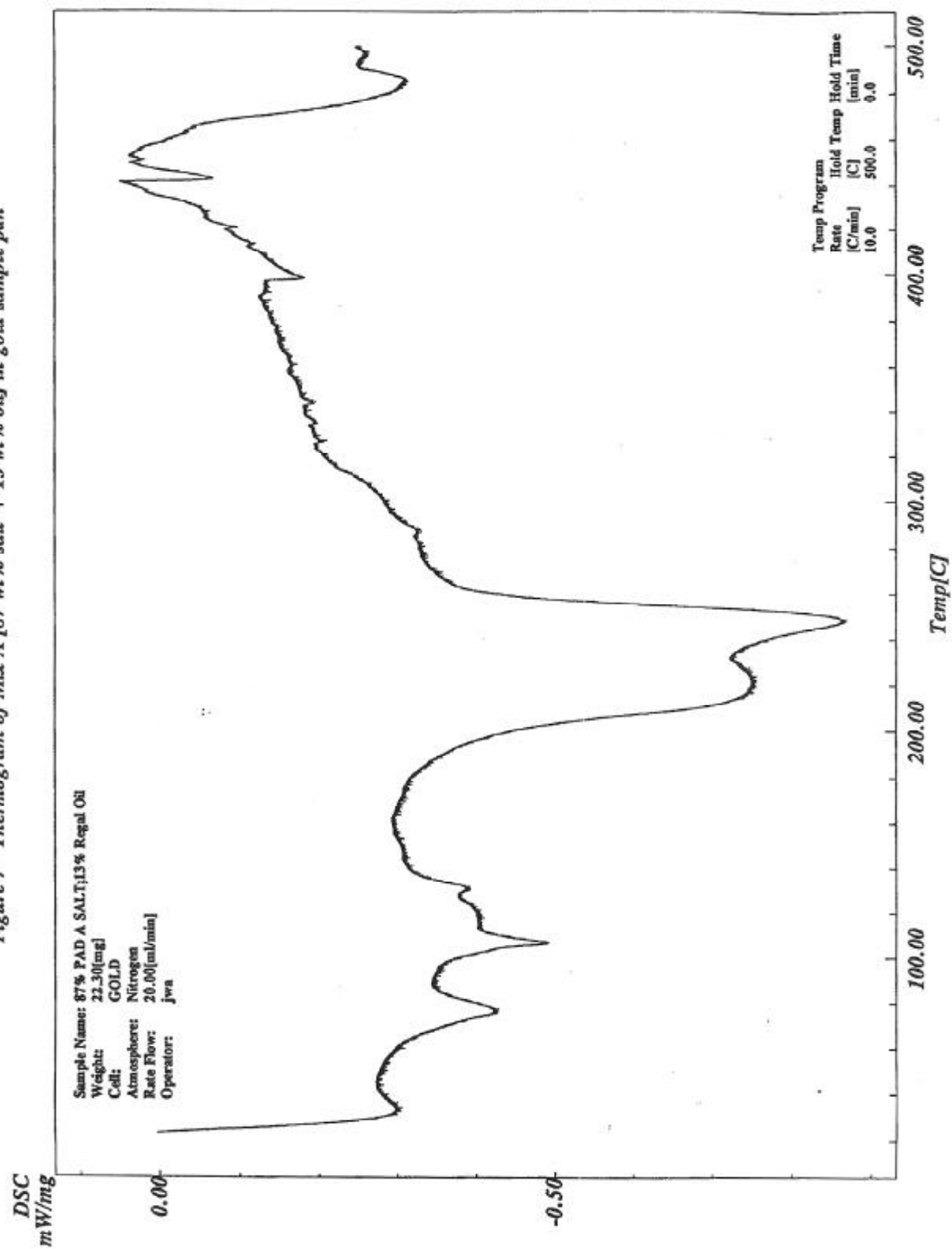


Figure 8 Thermogram of Mix B [91 wt% salt + 9 wt% oil] in gold sample pan

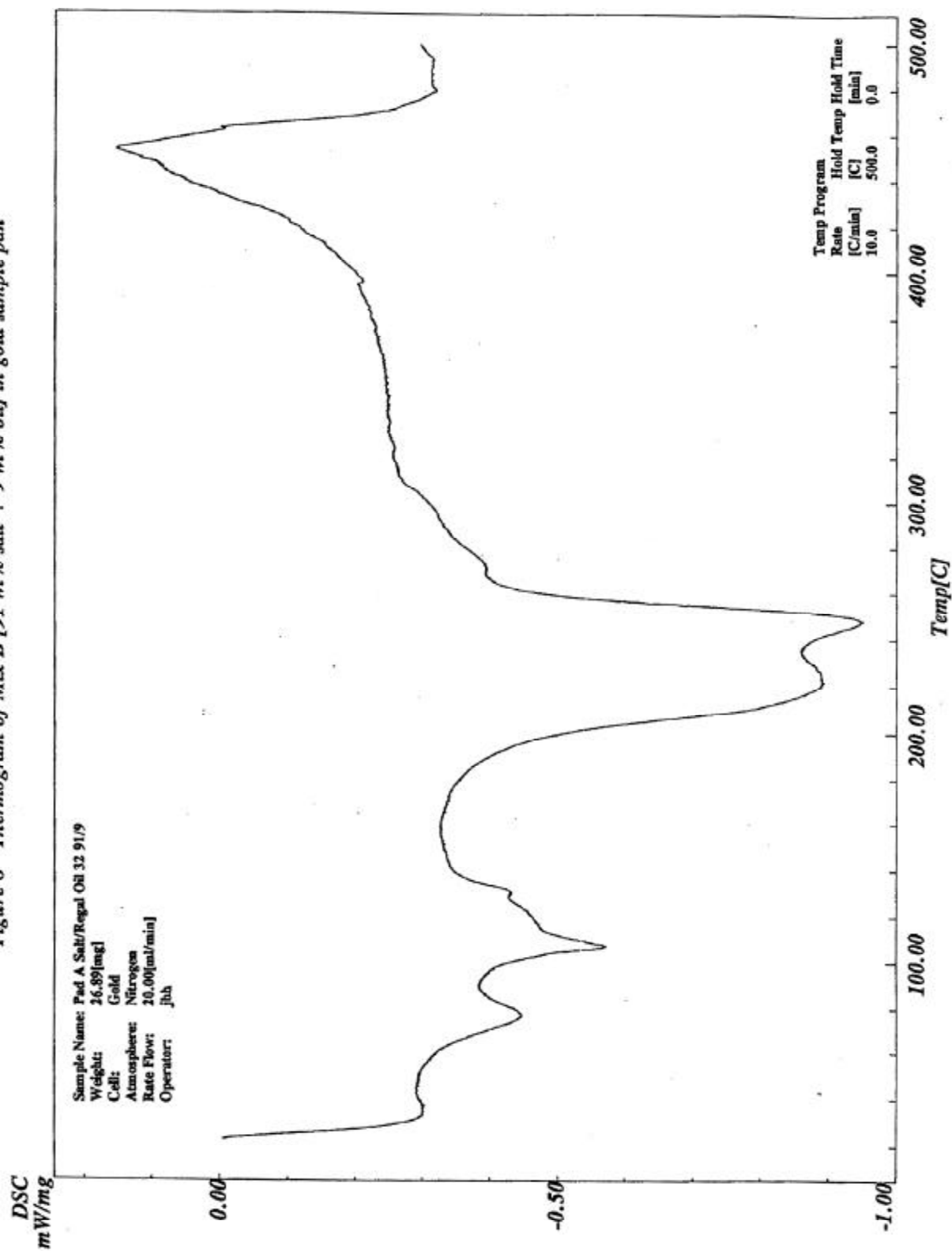


Figure 13 Thermograms of Mix A [87 wt% salt + 13 wt% oil]

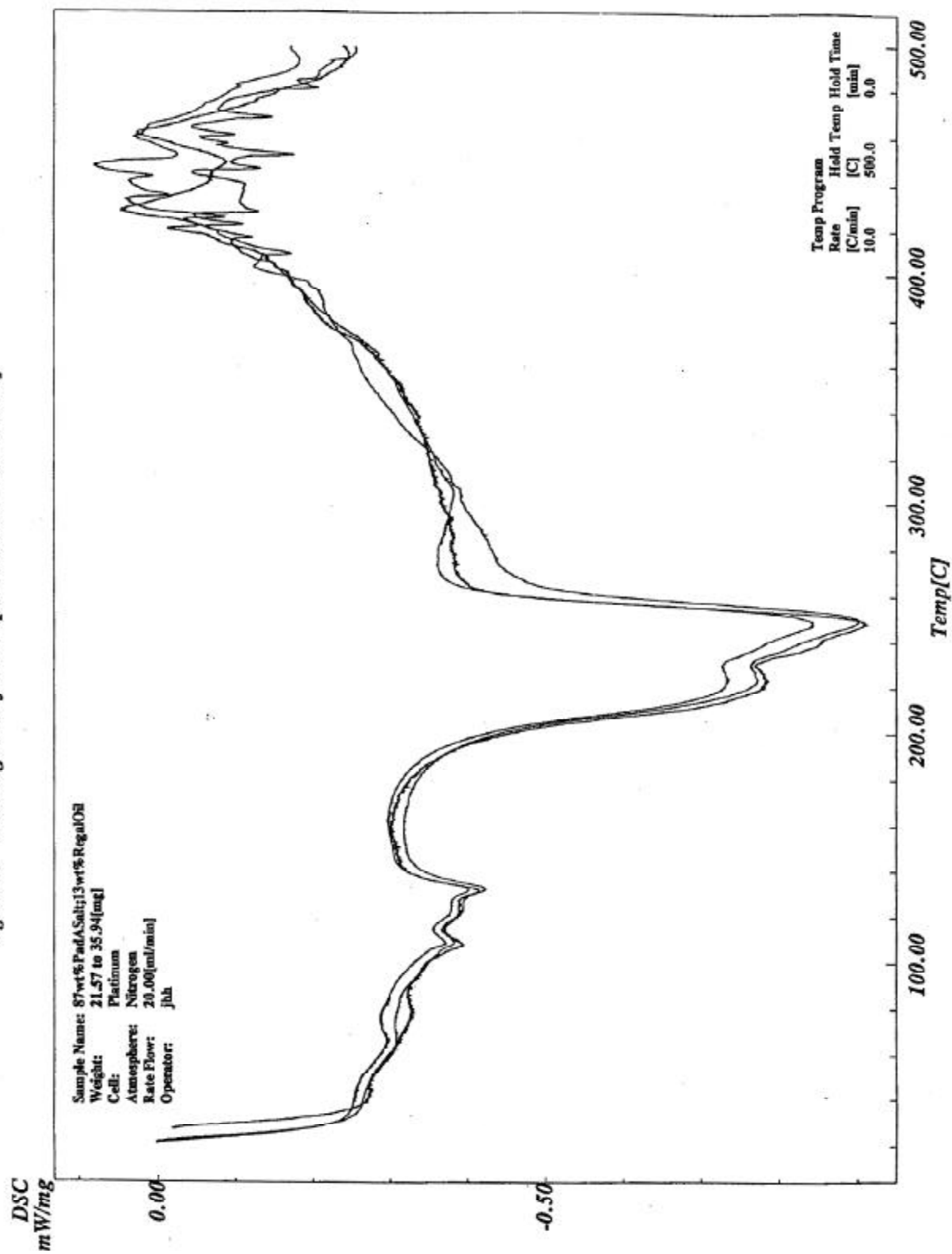


Figure 14 Thermograms of Mix B [91 wt% salt + 9 wt% oil]

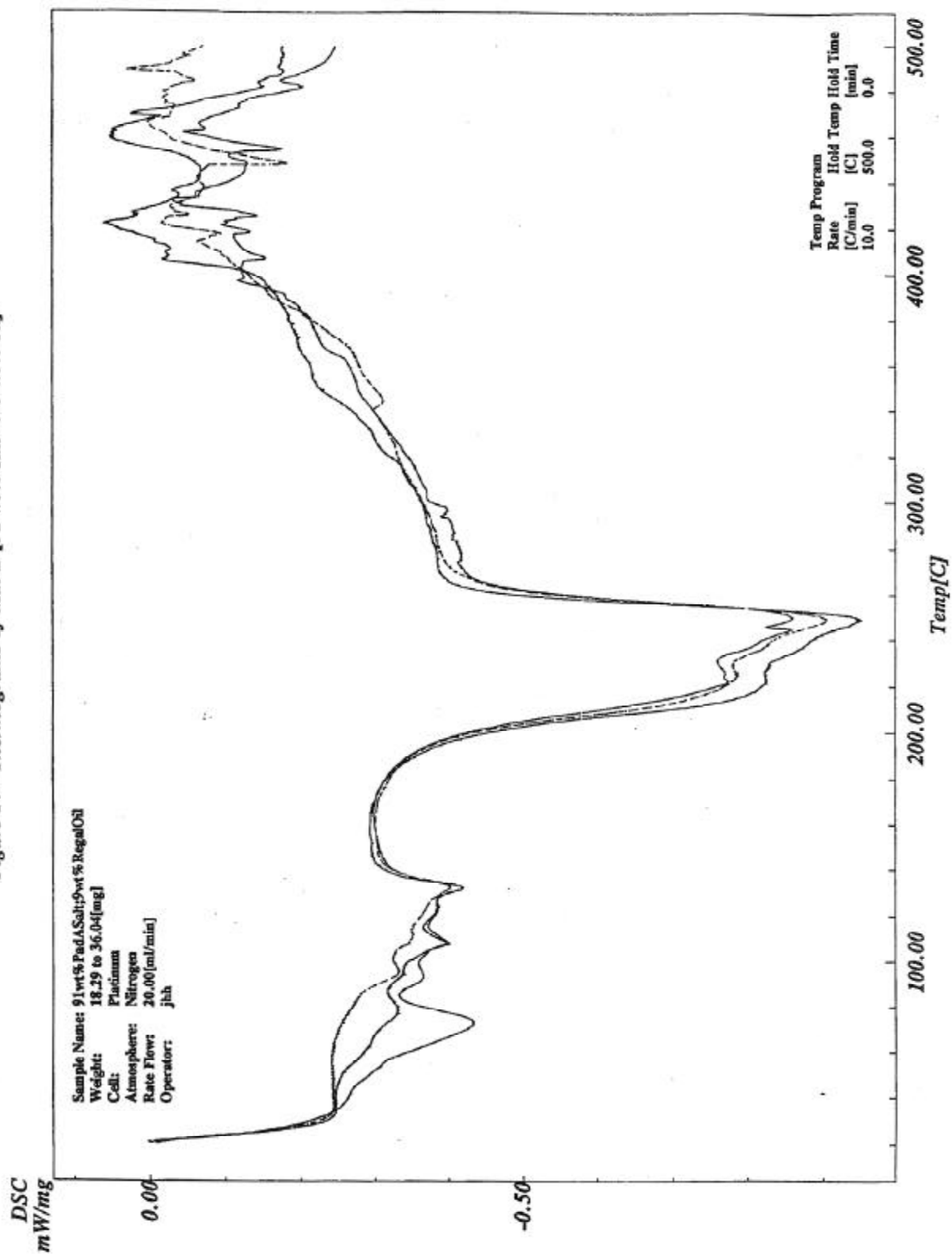


Figure 15 Thermograms of Mix A and Mix B

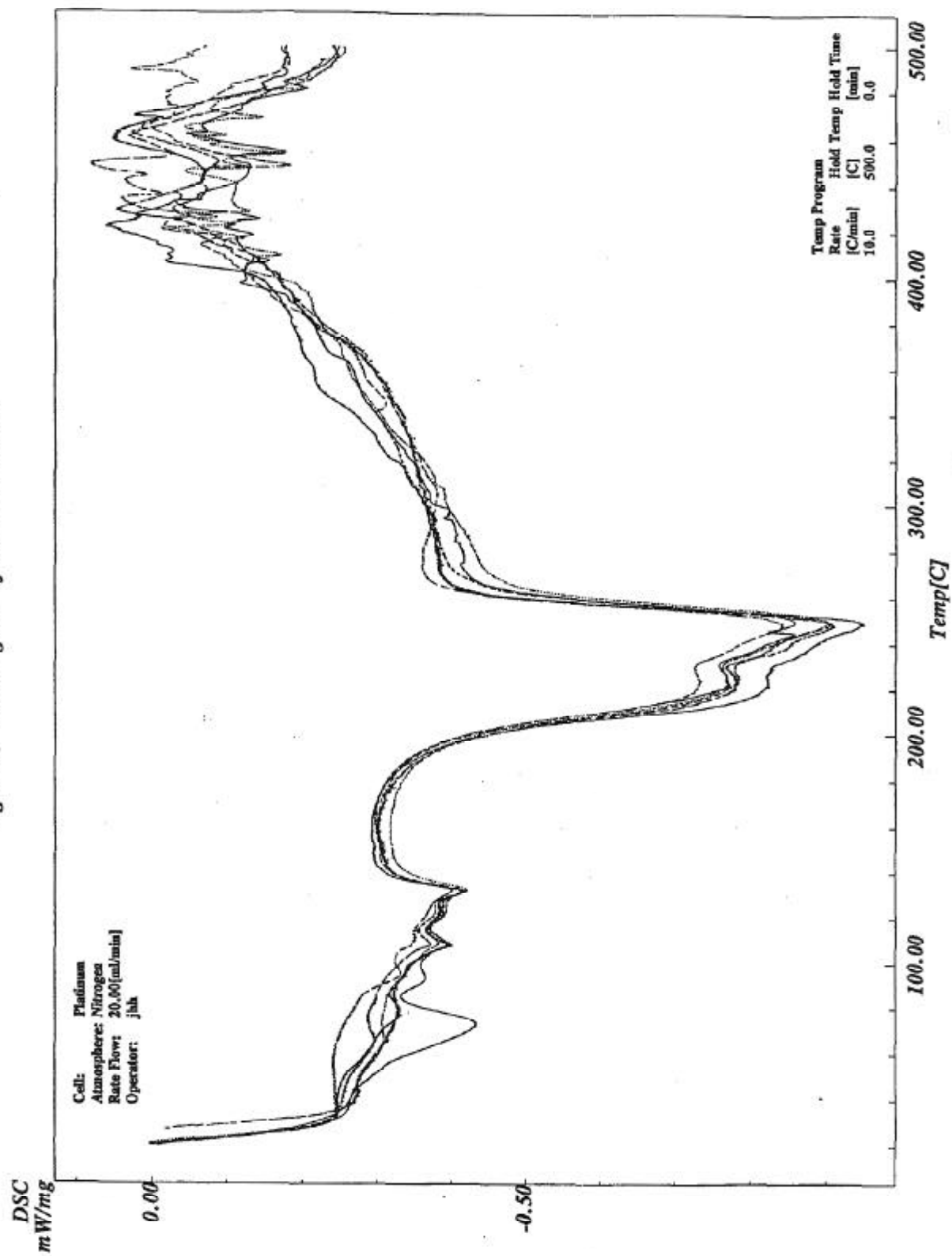


Figure 16 Thermograms of INEEL Pad A Salt, Regal Oil 32, Mix A and Mix B

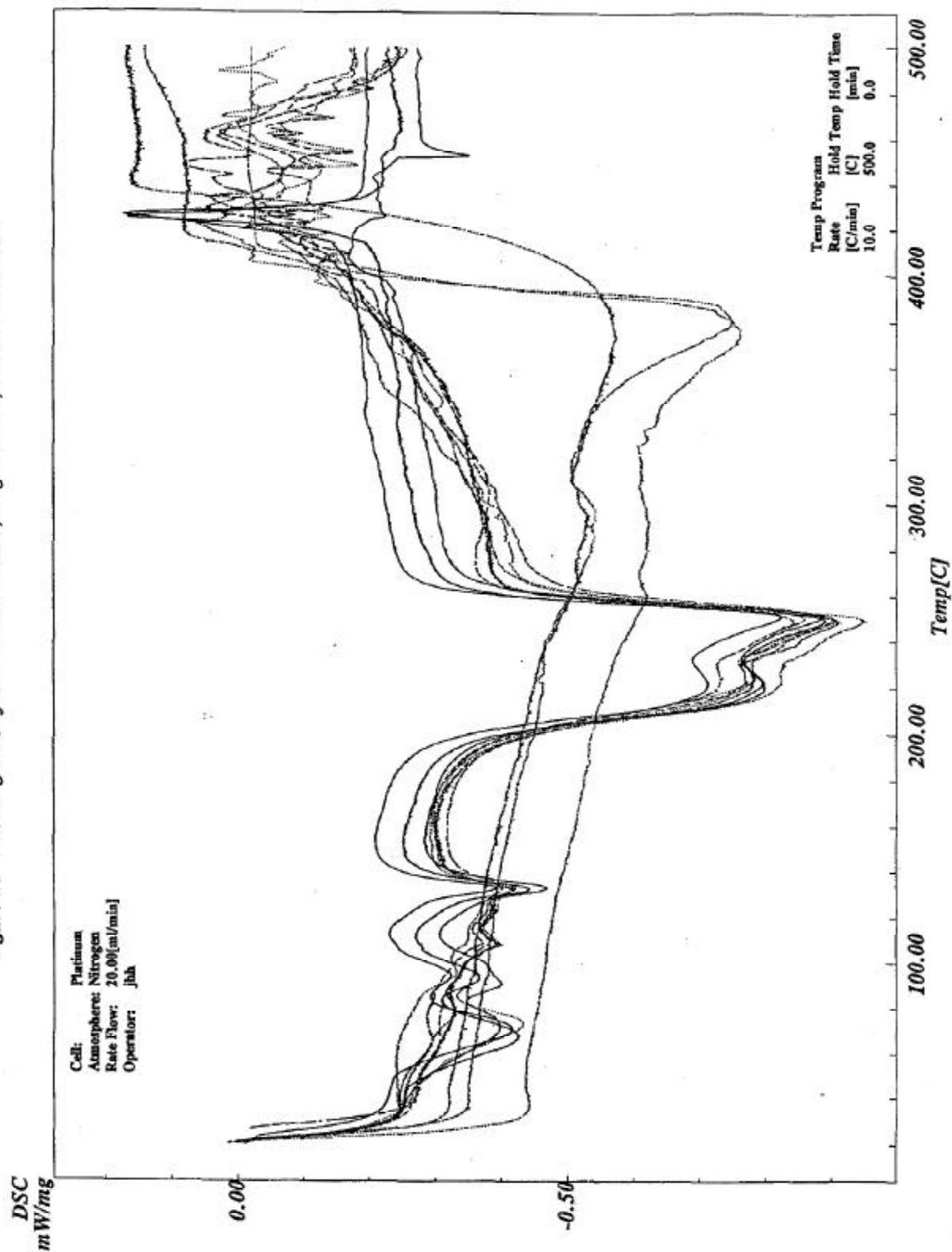


Figure 17 Thermograms of Spectroscopic Grade Graphite

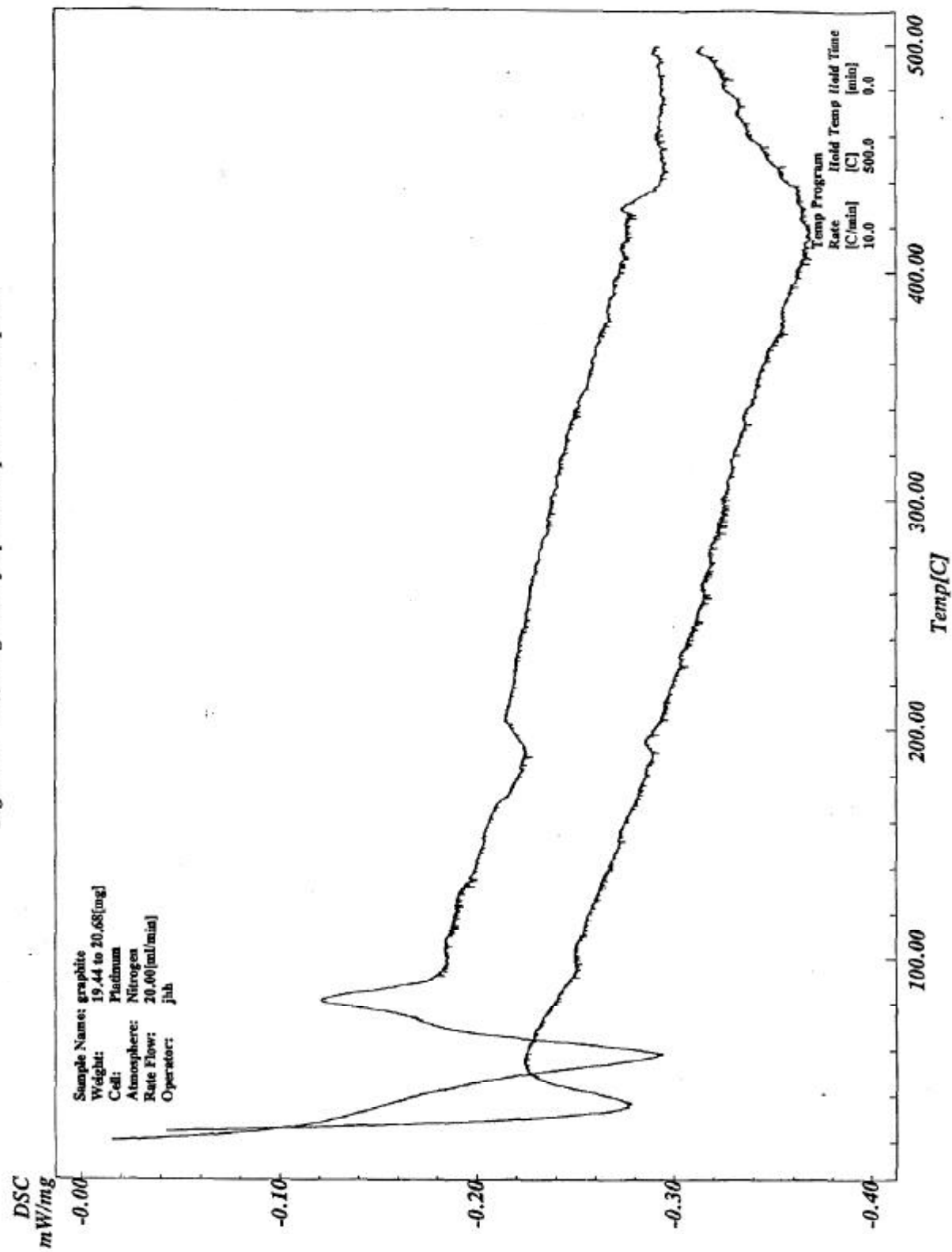


Figure 18 Thermograms of Sawdust

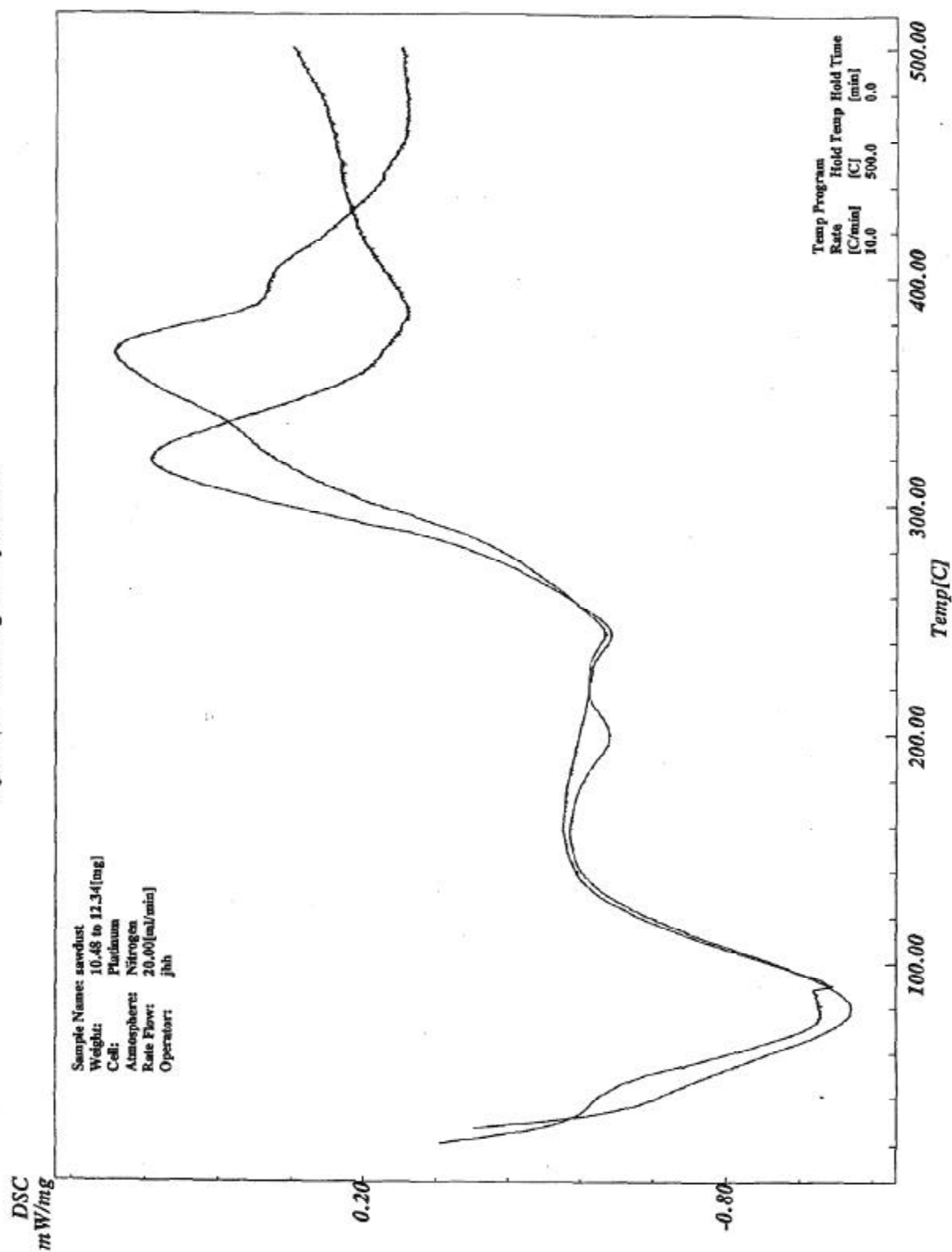


Figure 19 Thermograms of 87 wt% INEEL Pad A Salt + 13 wt% Graphite

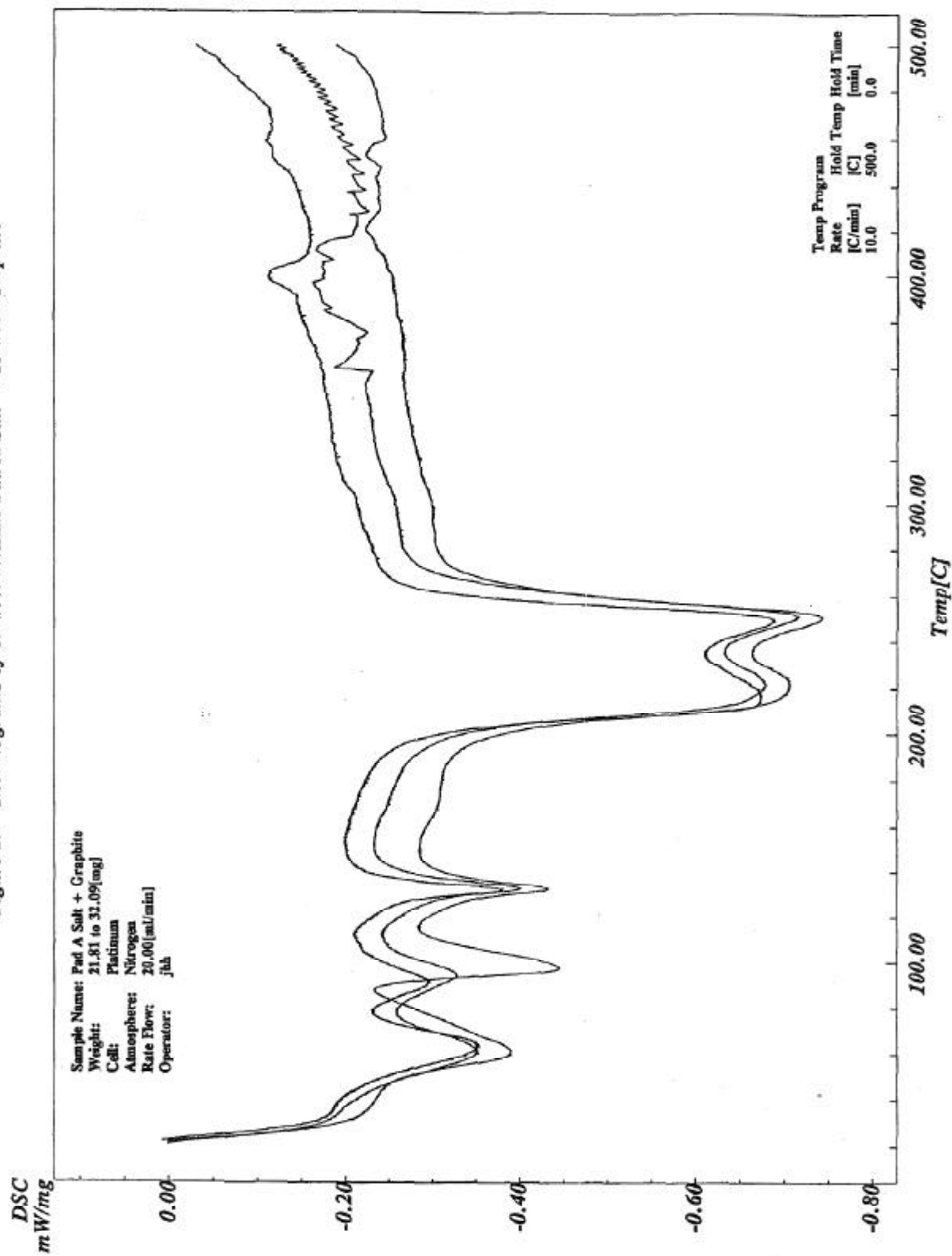


Figure 20 Thermograms of INEEL Pad A Salt, Graphite and the Stoichiometric Mix

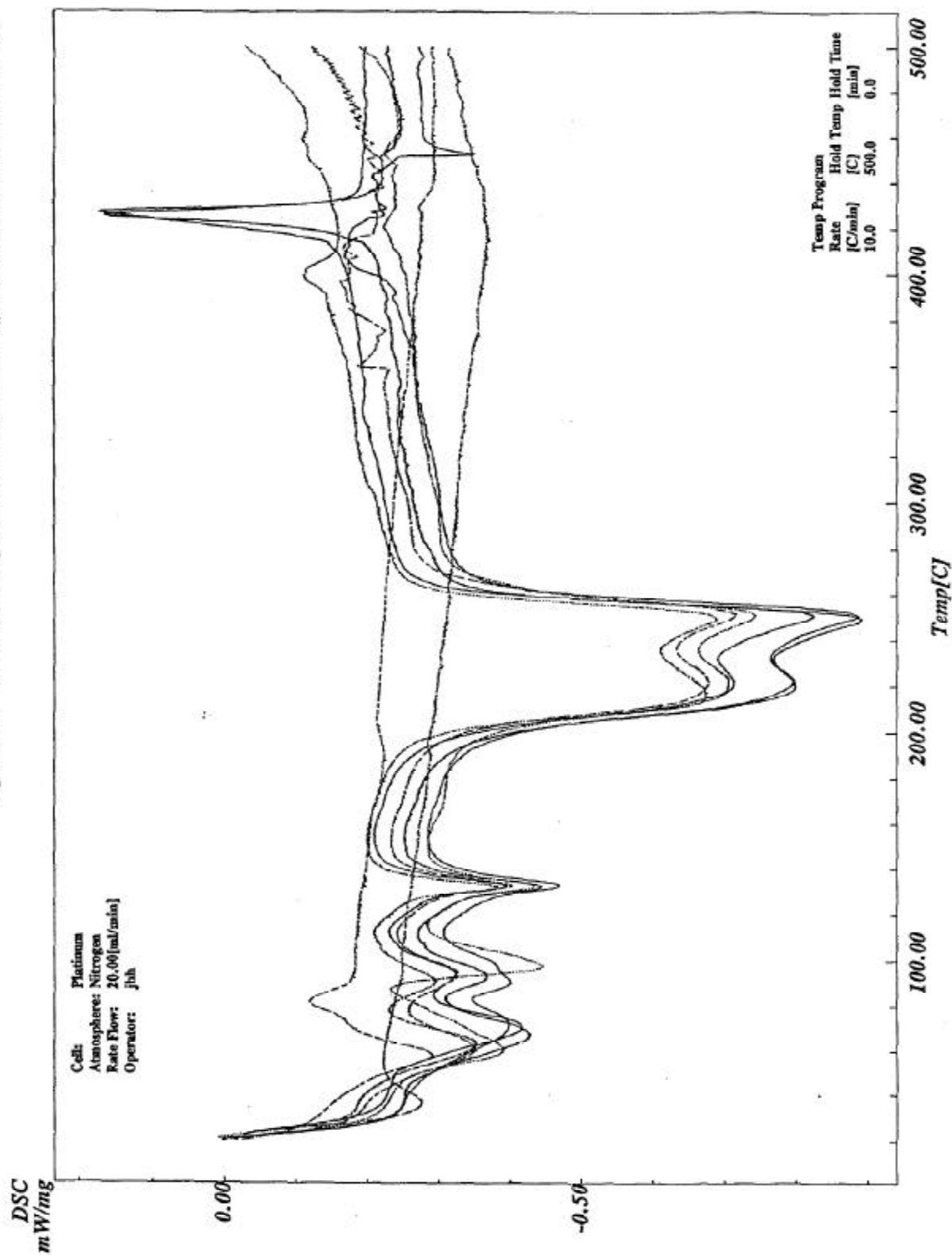


Figure 21 Thermograms of 87 wt% INEEL Pad A Salt + 13 wt% Sawdust

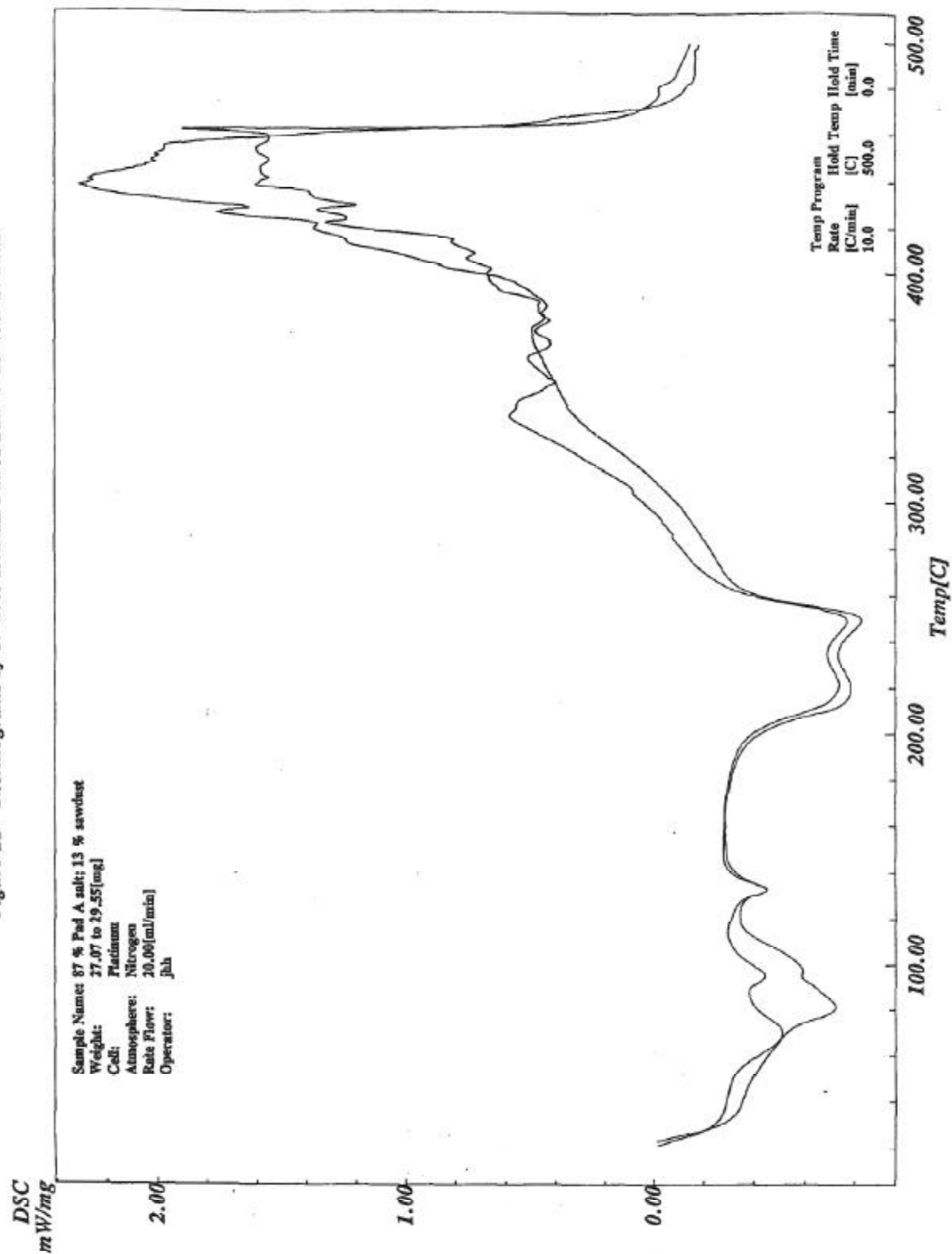
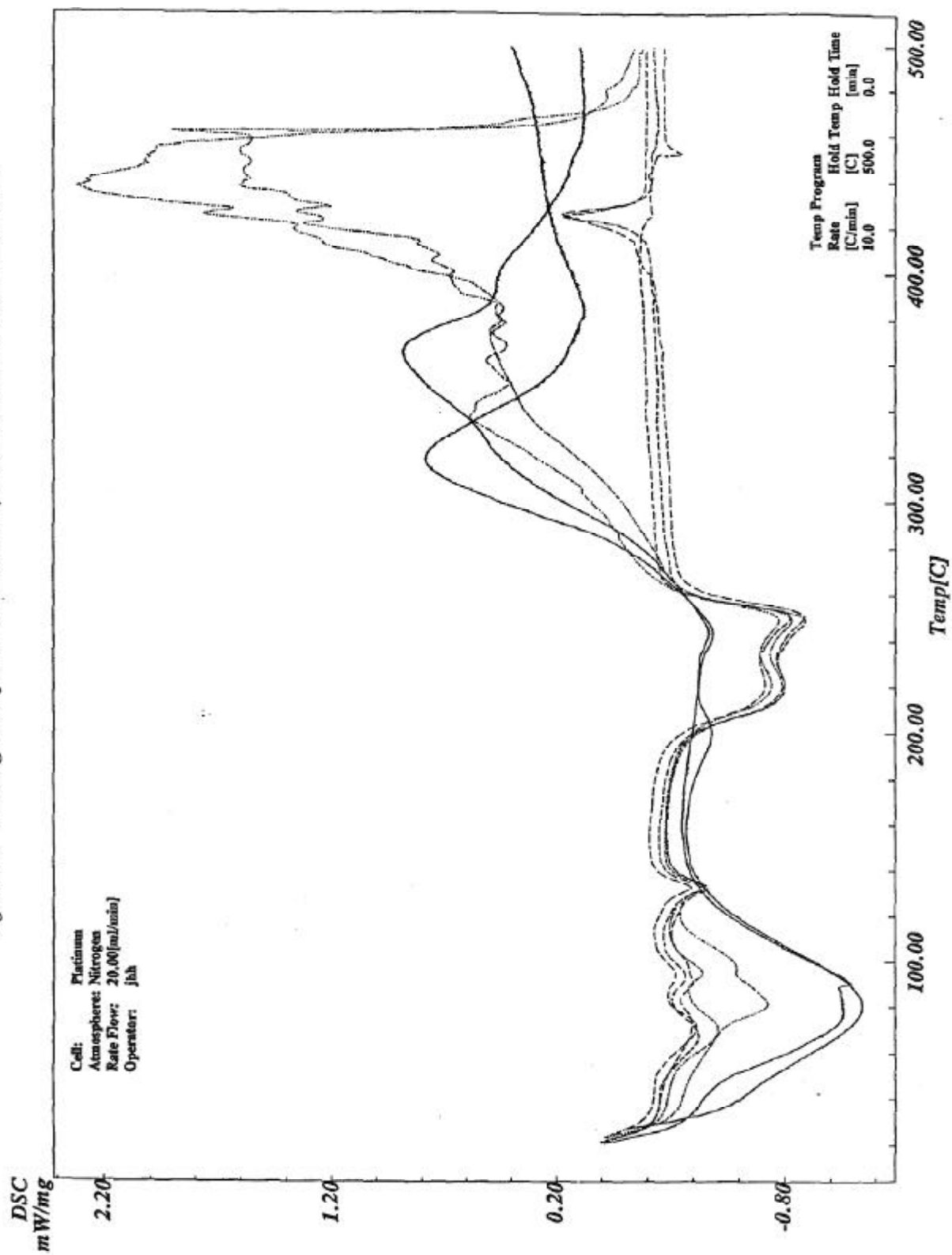


Figure 22 Thermograms of INEEL Pad A Salt, Sawdust and the Stoichiometric Mix



Test Report on Issue 001 for the Independent Technical Review Panel Nitrate Organic Reactivity Differential Scanning Calorimetry Results

1. INTRODUCTION

This report was prepared by LMITCO and Brookhaven National Lab (BNL) Environmental Waste Technology Center (EWTC). This report supports decisions related to safety issues that must be resolved prior to emplacement of probe holes as planned for the OU 7-10 Staged Interim Action, Stage I, Phase I.

Before Stage I coring into Pit 9, approximately 25 exploratory probe holes will be sonically drilled. Burial records indicate that 5% of the drums disposed of in that area contain Series 745 sludges (primarily nitrate salts). About 10% of the drums were the Series 743 sludges (primarily clay absorbent and lathe coolant- carbon tetrachloride and machine oil). The Independent Technical Review Panel (ITRP) requested information on the reactivity of these two waste streams.

A 55-gallon drum was retrieved in 1988 from storage in Pad A at the INEEL's Radioactive Waste Management Complex. A sample of the Series 745 sludge was taken in 1991 from this drum and extensively characterized for a treatability study. A sub sample of the drum contents was retrieved from its current storage site and sent to Brookhaven National Laboratory and subjected to differential scanning calorimeter (DSC) tests.

The organic used in these tests was Texaco Regal Oil 32. This oil is typical of the machine oils used as part of the lathe coolant portion of the sludge waste. This oil accounts for 20.5 vol.% (13.3 wt.%) of the organic content of the 743 sludge liquids. Fully 68.7 vol.% (79.8 wt.%) of the organic liquids are inert (to nitrate reactivity) chlorinated hydrocarbons.

The DSC results from salt oil mixtures are reported in this document.

2. BACKGROUND

The safety issues relate to the potential exothermic reactions between alkali nitrate salts and organic materials disposed of in Pit 9. An earlier report (Beitel 1999) identified six factors necessary to supporting uncontrolled reactivity in mixtures of alkali nitrates and organic materials. These factors are:

1. Physical configuration
2. Oxidizer fuel composition and ratio
3. Moisture content
4. Mixture
5. Mass
6. Ignition source –
 - a. Temperature, or,
 - b. Shock.

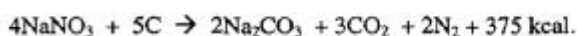
The proposed tests were based on a concern that oil, which is present in the waste at relatively large volumes, could conceivably, passively mix uniformly with the alkali nitrates. If such mixtures could react exothermically there could be an additional safety problem.

2.1 Composition of Oils, Nitrate Salts, and Mixtures

The chemical analysis of the Pad A salt shows **55 wt.% nitrate, 20% sodium, 7.6% potassium, 3.6% sulfate 2.1% chloride 1.8 % water 1.4% phosphate 1% organic carbon, 0.6% fluoride, 0.3 % nitrite, 0.2% calcium, 0.1 % lithium.** The alkali nitrate salt ingredients are in **bold**. A radionuclide analysis shows that it contains approximately 185 pCi/g Uranium, 0.3 pCi/g Pu-239, 0.3 pCi/g Am-241, 0.1 pCi/g Cs-137, and 74 pCi/g K-40. The bulk density as packaged in the drum was 0.77 g/cc compared to a specific gravity for example of sodium nitrate of 2.26. The salts look like "Rice Krispies", mostly off-white with some yellowish crystals (Shaw 1993).

The oils used at RFP are no longer manufactured. Oils with the same name are made that have been improved and modified in 30 years. The best currently available substitute, Texaco Regal-R&O-32 was used as a surrogate of this oil that is part of the 743 sludge matrix. Texaco Regal-R&O-32 is a light paraffinic mineral oil with a viscosity of 32 centistokes, containing 0.5 wt.% 2,4,6 – tris (tert-butyl) phenol as an antioxidant additive. The oil is reported to have an approximate molecular weight over 360, a specific gravity of 0.87, is straight chained fully saturated with a formula of $(CH_2)_n$. Thus 12/14 or 86% of the mass is carbon. The flash point is 200°C.

The generic reaction between sodium nitrate and pure carbon proceeds according to the following equation:



In this reaction, 340 g of sodium nitrate reacts with 60 grams of carbon. The stoichiometric ratio of nitrate to carbon is 85:15. Instead of pure carbon (charcoal, coal, or carbon black,) we have the paraffinic oil, which is 86% carbon. Since the nitrate salts are only 83% alkali oxidizers ($55+20+7.6+0.3+0.1$), it requires only 13% by weight oil for a stoichiometric carbon equivalent. A sub-stoichiometric ratio of 91%-9% oil was also used for the nitrate rich case.

2.2 Physical Configuration and Mixing

Since the nitrates disposed of in Pit 9 were originally packaged at RFP separate from any significant quantities of any organic material that could act as a fuel, there could be no reactions without a mixing mechanism. Oils used at the plant were also packaged at RFP in the "grease plant" by mixing with a clay absorbent. Though a remote possibility and hard to envision on any macro scale there is a postulated passive mixing mechanism of the oils with nitrate salts.

This mechanism requires first that the oils separate from the "grease-like" absorbent matrix, separate from the carbon tetrachloride dissolved in it, move out of the drum "en mass" through gravitational or capillary flow, and into a nitrate salt drum, without dilution by water or contamination by soil. The oil would then have to intimately mix with the nitrates. Some liquid/solid separation has been observed in stored above ground Series 743 sludge mixtures.

However, the oil must not only separate from the absorbent but also from the chlorinated solvents within each drum and then move out of the drum, by ordinary environmental processes, for any exothermic reaction with the nitrates to be considered possible. The difficulty of this separation is indicated by the failure of an extensive program in the early 1960's to do this, separate the chlorinated solvent from the oil. This failure led to the "grease plant" approach, which resulted in the current 743 sludges.

Various degrees of drum deterioration have been observed in the Early Waste Retrieval. Most of the drums were breached (not pressure tight) but were still intact (able to be placed as a single container in an overpack). If oil nitrate salt mixtures are reactive, then penetration by the sonic drill could initiate that reaction. Any reactivity might invalidate some of the conclusions of EDF-ER-060.

2.3 Temperature

The ignition temperatures for organics with nitrate salts usually occur between melting and the decomposition temperature. The melting temperature of sodium nitrate is 306°C, potassium nitrate is 334°C. The decomposition temperature is 380°C for sodium nitrate and 400°C for potassium nitrate. When these salts are combined a eutectic is formed which depresses the melting point to 250°C and also seems to lower the decomposition point to 350°C.

3. THEORY OF DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetry (DSC) is a thermal analytical technique used to characterize specific heat and enthalpies of transition, of a sample relative to a reference material. In DSC, the sample and reference substances are heated in separate holders. Temperatures of the two materials are controlled by average temperature circuits to match a pre-determined temperature ramp (programmed time-temperature). A differential temperature circuit measures the small differences between the sample and reference holders and proportions the power to each holder to keep the temperatures equivalent. The difference in power is proportional to the heat absorbed or evolved by the sample (e.g., during transition such as melting or crystal phase changes, during endothermic or exothermic reactions).

In this case the temperatures was measured to ± 0.5 degree Celsius as the reference is raised 2 or 10 degree/minute from 25 to 400°C. The electrical energy required to maintain both materials at the same temperature is recorded on the y-axis (see Figure 1-6) of each scan versus temperature rise on the x-axis.

A negative peak occurs when more heat is absorbed (more outside electrical energy required to maintain temperature) in test sample than in the reference sample; this indicates an endothermic transformation in the sample. Endotherms are typically due to physical changes such as melting, phase transition and vaporization and chemical changes such as pyrolysis and some decomposition. A positive peak indicates an exothermic reaction, heat is given off (less outside electrical energy required to maintain temperature) in the test sample. Exothermic transformations include chemical reactions such as combustion and some decomposition and recrystallization.

4. EXPERIMENTAL

The objective of the DSC tests was to verify the absence of exothermic reactions between RFP Series 745 "salt" and oil that might be mixed and might be encountered during probing and coring activities. The Environmental & Waste Management Group (EWMG) at Brookhaven National laboratory (BNL) used DSC to analyze Pad A salt (RFP Series 745 Sludge) and assess interactions between the Pad A waste and Regal 32 Oil.

Testing was performed in accordance to ASTM method E-537, "Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis."

The following samples were prepared and DSC tested.

- Pad A salt (RFP Series 745 sludge)
- Texaco Regal Oil.
- Salt plus a stoichiometric amount of oil added (87 wt-% salt and 13 wt-% oil).
- Salt plus 70% of the stoichiometric amount of oil (91 wt-% salt and 9 wt-% oil).

Between 40 and 60 mg of each material or mix was loaded into individual 6 mm diameter aluminum (high pressure) gold (low pressure) or platinum (covered but not sealed) pans Replicates are run on the Pad A salt, and salt-Texaco Regal oil 32 oil mixtures. Samples for the two oil-nitrate salts mixtures were prepared by weighing 0.04-0.05 g of salt into the crucible then adding the required amount of oil, 40-60 microliters, by micro-pipette onto it to reach the required composition.

Both salt and oil mixtures were prepared a macro amount (~1 gram) and a sub sample of this was taken for DSC analysis. The mix was prepared by weighing out the salt and oil into a clean and dry, glazed crucible and mixing with a Teflon spatula for 2 minutes. This was done to be certain that intimate mixing of the oil and salt occurred.

Sealed sample containers made of aluminum pans, which were subsequently sealed, with aluminum covers capable of handling up to 750 psi of pressure were initially used. Replicate samples of each material were prepared and tested using a Shimadzu DSC-50. Test runs were performed from 25°C to 400°C at a heating rate of 2°C/min. The furnace atmosphere was nitrogen gas flowing at approximately 20 cc/min. The reference material for each run was an identically prepared empty aluminum cell.

However, in analyzing initial test results, it was observed these aluminum crucibles reacted with the nitrate as it decomposed at the higher temperatures. Results of running the salt alone showed exothermic reactions between the high-pressure aluminum pan and salt occurring between 300°C and 400°C (see Figure 3).

The materials were then re-run using gold pans. These pans, while crimp-sealed, were capable of withstanding internal pressures of about 15 psi. When these pans were exhausted, regular covered platinum pans were used operating at the ambient atmospheric pressure. Runs were performed at 10°C/min to increase the mW/mg-min and gain better sensitivity on the fine details.

5. RESULTS

The experimental results are shown in the six attached DSC scans.

There are no exotherms in any of the runs up to 430°C. The results (Figure 1) for the Pad A salt waste alone showed a clean thermogram with only endothermic peaks. Peaks occur at the expected locations. There are two peaks below 100°C that correspond to the loss of water of hydration for sodium sulfate [10 H₂O and 7 H₂O]. Following this is the transition peak for potassium nitrate [129°C] and the composite melting point peaks for sodium and potassium nitrates. These melting points are depressed to 200°C to 260°C as opposed to referenced melting points for the individual salts of 306°C and 334°C for sodium nitrate and potassium nitrate respectively.

The only notable differences are the first two peaks that are assigned to water loss from hydrates are shifted slightly higher in temperature. This would be expected as the oil coating the salt should slow dehydration processes. The composite melting point is in the same position in the mix as in the salt alone thermogram. Since the oil evaporates completely by 320°C, no reaction between salt and oil would be noted above this temperature under normal atmospheric pressures. A broad, apparent exotherm is visible on one scan above.

These thermogram characteristics are similar to thermograms of RFP surrogate salt waste tested at BNL in the late 1980s where this same lowered eutectic melting point was noted. Also past DSC salt-(RFP surrogate) organic(polyethylene and polyester-styrene) scans compare favorably with these actual salt and oil mixtures.

The 91/9-wt.% mix of Pad A Salt/Regal 32 Oil was similar to the 87/13-wt.% mix. No exothermic reactions were noted for either material. Again, it should be pointed out that these are atmospheric pressure runs and the oil might have evaporated out by 320°C. DSC tests were conducted in sealed capsules to prevent this vaporization and separation of the oil from the nitrate prior to reaching a temperature at which an exothermic reaction may occur. This effort was not entirely successful due to reaction of the oil with the pan itself (Fig 3).

The Pad salts exhibit no exotherms up to 500°C with a flat baseline (Fig. 1). The 87/13 scan available (Fig. 2) exhibits a steadily rising baseline after melting culminating in a broad peak at 450°C. Further scans (not available at this time) indicate this is a baseline problem with the equipment.

For the oil-salt mixtures the melting point is 220-250°C. In an unconfined crucible, the oil boils at about 320°C and is gone (flat curve) by 360°C (Fig. 4). At elevated temperatures (480°C) and pressure (750 psi), decomposition or boiling occurs (see sharp endotherm in Fig. 5). Both the 9% and 13% oil mixtures are similar with the same melting point as the pure salt.

You can see the melting point of nitrite in the pure salt curve at 212-218°C. A micro-mix in the crucible does not seem to affect the results when compared to a 9% and 13% macro mix (gram quantities rather than mg quantities in the reaction crucible). This data was collected, but not in time to include a hard copy of the scan.

The DSCs test samples were run against an inert standard. Temperature was ramped 25 to 400°C at 2 °C/minute for the sealed capsules and 10 °C/minute with the unsealed. The melting point endotherm is 218 - 248 °C for the salts alone, and 212-248°C for the salt-oil mixture. At 200°C temperature the alkali nitrate salts begin to melt with melting complete by 260°C for both the salt and the oil-salt mixtures. A specific decomposition endotherm was not noted. The oil and salt raise the boiling point of water slightly to 105-130°C.

The thermogram for the Texaco Regal Oil 32 is depicted in Figure 4-6 using different crucibles and an extended temperature range. The oil shows a broad boiling point endothermic peak centered around 320°C. The broad nature of the peak is as expected for an oil distillate. The oil was completely evaporated away by 360°C. The oil run in a 50 atmosphere sealed aluminum pan is presented in Figure 6 for comparison.

The oil absorbs on the nitrate salts but does not dissolve it. There appears to be no shift in the nitrate salt melting point (largest endotherm) due to the oil. The nitrate salt sample starts to decompose in the crucible before the test is complete but the oil does not totally vaporize if under pressure by that time. The pressurization of the crucibles does not seem to change the appearance of the calorimetry scans.

6. CONCLUSION

- No exothermic reactions are observed in the Pad salts themselves.
 - The 0.9% organic, 0.3% nitrites are insufficient to cause any reactivity.
 - Waters-of-hydration and crystallization give small endotherms.
- No exothermic reaction observed from either the 9% or 13% oil-salt mixtures below 400°C.
 - The two different compositions give identical scans for a given crucible material (two different crucible materials are shown).
 - Below 350°C (before crucible material interference) pressure does not change reactivity of this mixture.
- The presence of an exothermic reaction can not be excluded for the 13% oil-salt mixture above 400°C on the scan available. A single subsequent scan, not available for this report failed to show the exotherm.
- The melting points of the mixtures and salts are the same. No shift observed in the melting point of the salt due to the presence of oil.
- The oil does not dissolve the nitrate but is absorbed onto it such that it does not drip from the nitrate.
- The oil is thermally very stable.
 - Boils at 320°C at atmospheric pressure.

- Boils at 480°C at elevated pressure.
- The moisture of the salt is the same now as when it was analyzed 8 years ago (1.8 wt.%).
- The particle size and appearance of the salts are the same as previously reported (Shaw 1993), yellow and white color and a course grainy, approximately 1-mm particles.

Experimental Data

The attached four figures present the experimental DSC scans. Figures were faxed to LMITCO with fax date and time indicated on each scan. The fax date corresponds to the test date

Figure 1. Pad A Salt Only in Gold Cell.

Figure 2. Salt and Oil (87/13) in Gold Cell.

Figure 3. Salt and Oil (91/9) in Aluminum Cell.

Figure 4. Oil Only in Gold Cell.

Figure 5. Oil Only in Platinum Cell.

Figure 6. Oil Only in Aluminum Cell.

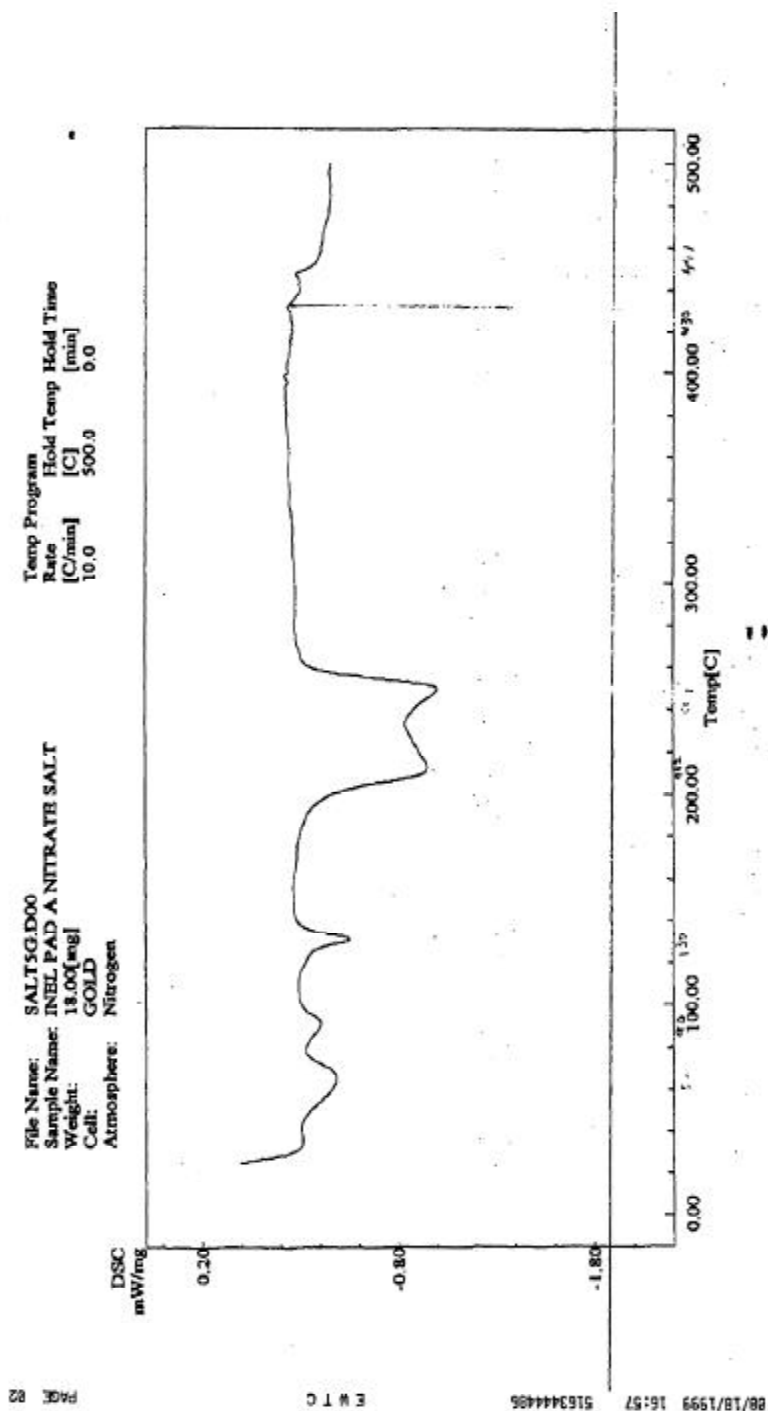


Figure 1. Pad A Salt Only in Gold Cell.

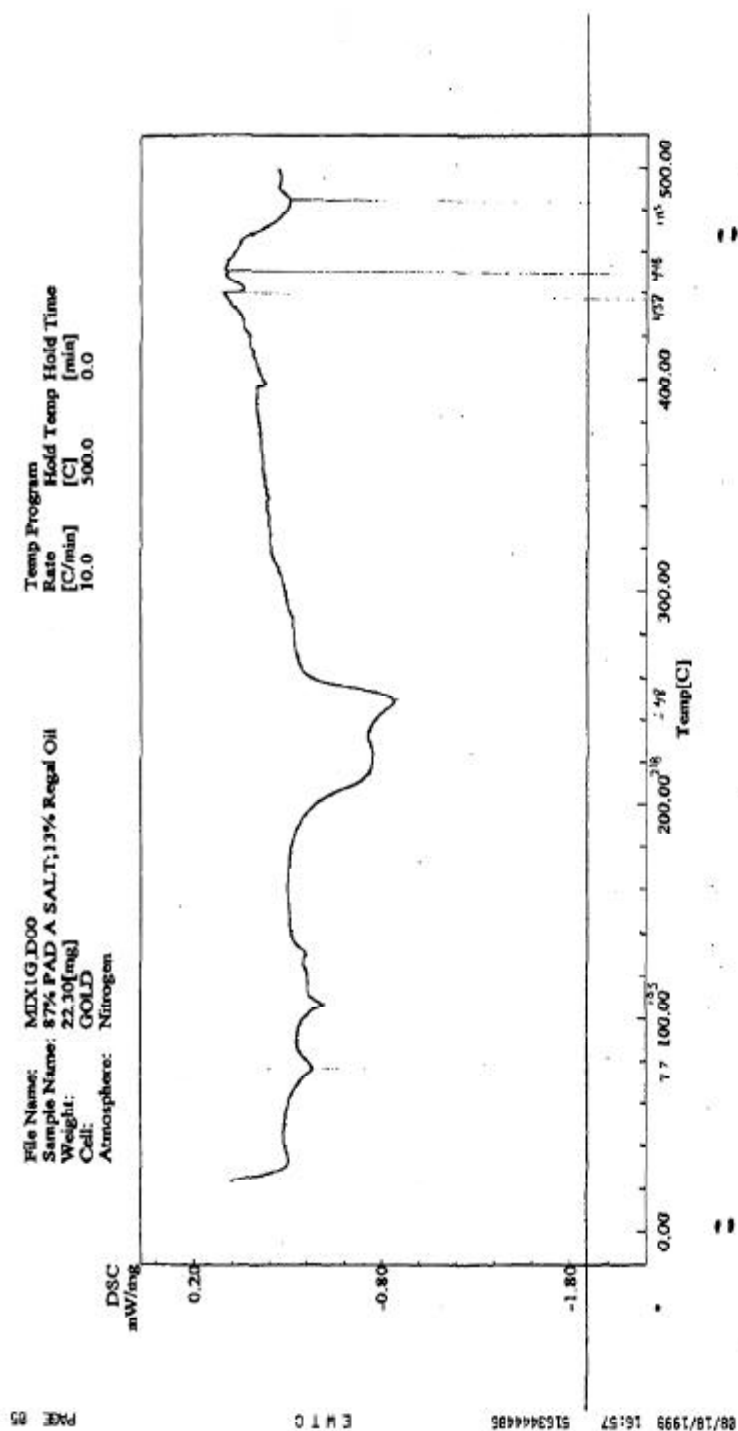


Figure 2. Salt and Oil (87/13) in Gold Cell.

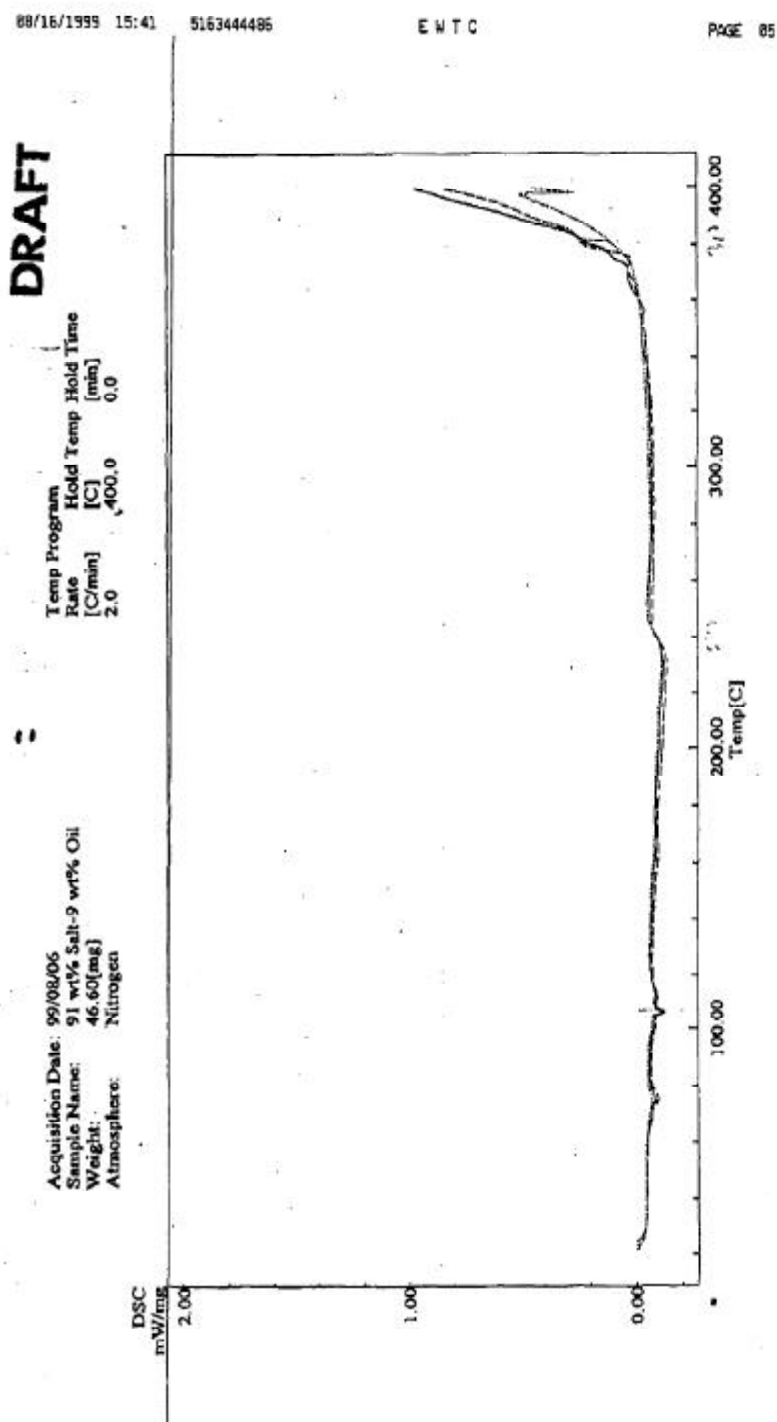


Figure 3. Salt and Oil (91/9) in Aluminum Cell.

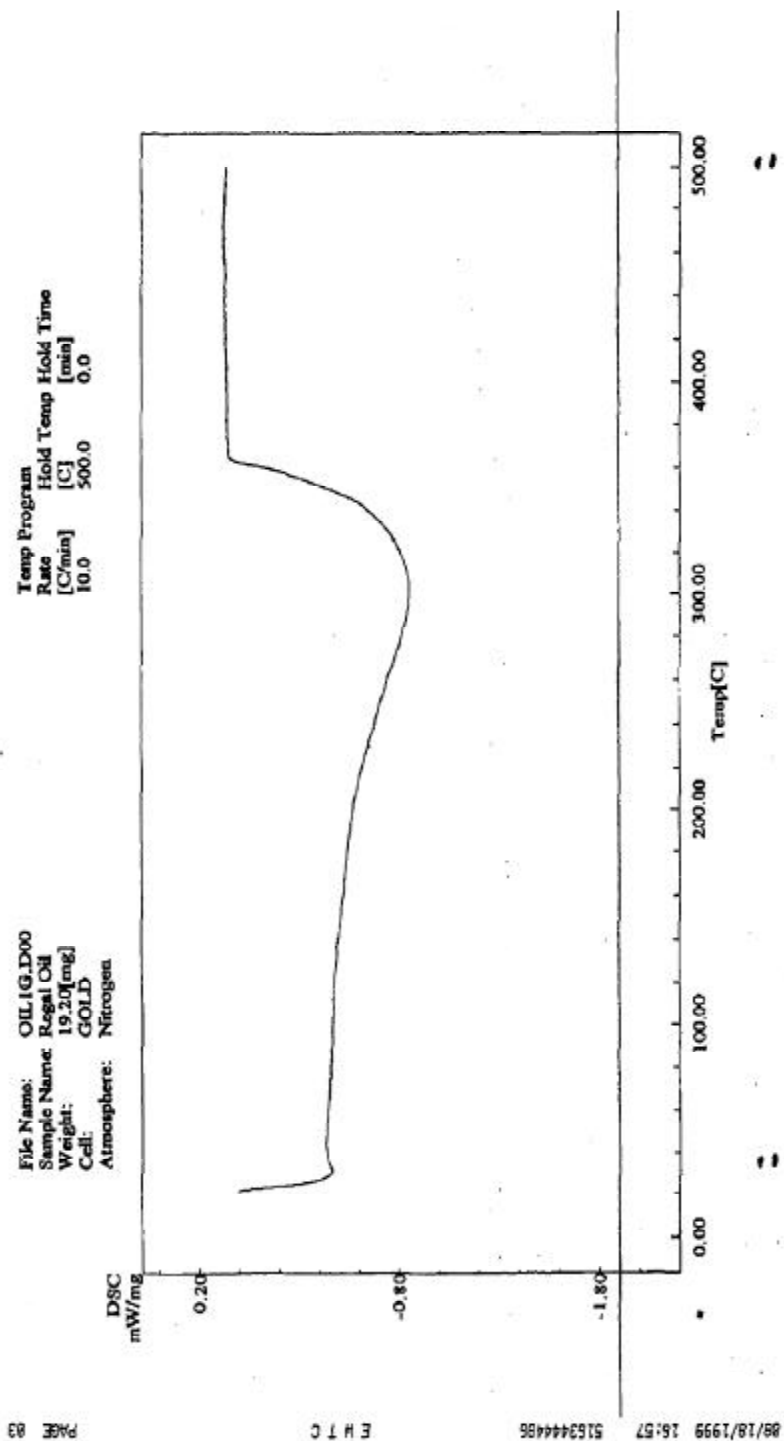


Figure 4. Oil Only in Gold Cell.

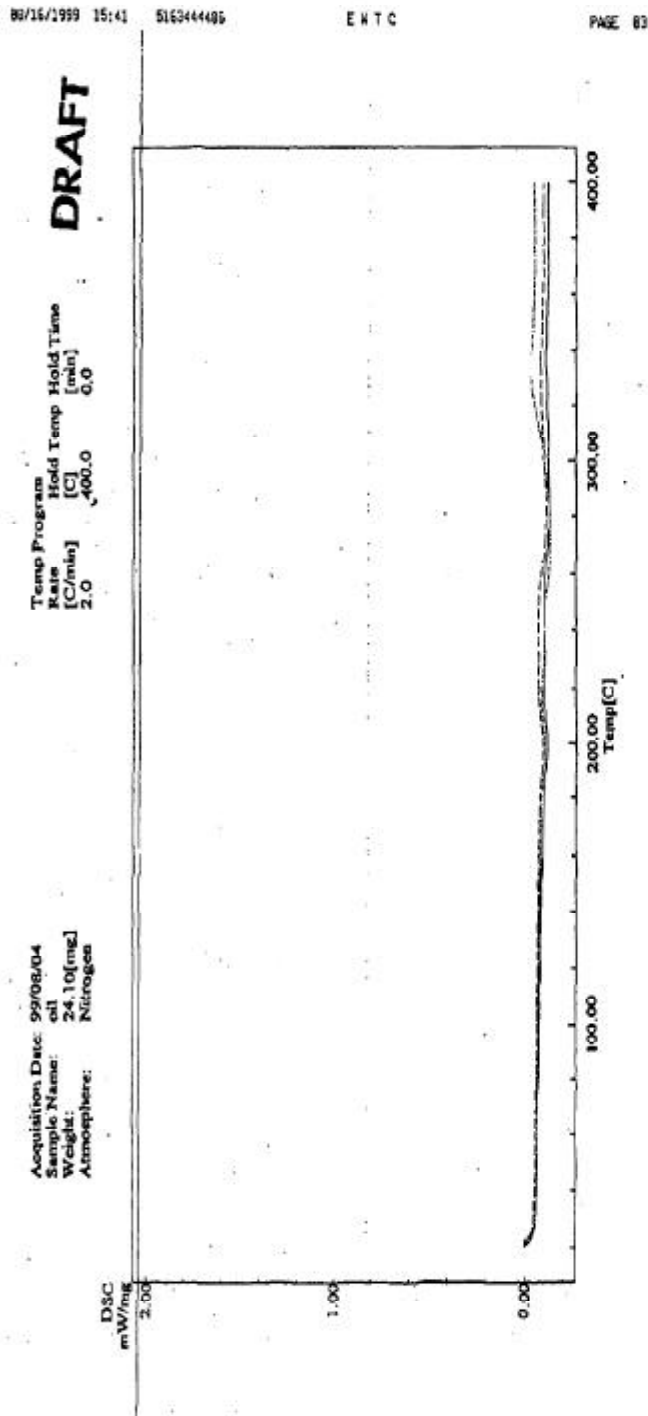


Figure 5. Oil Only in Platinum Cell.

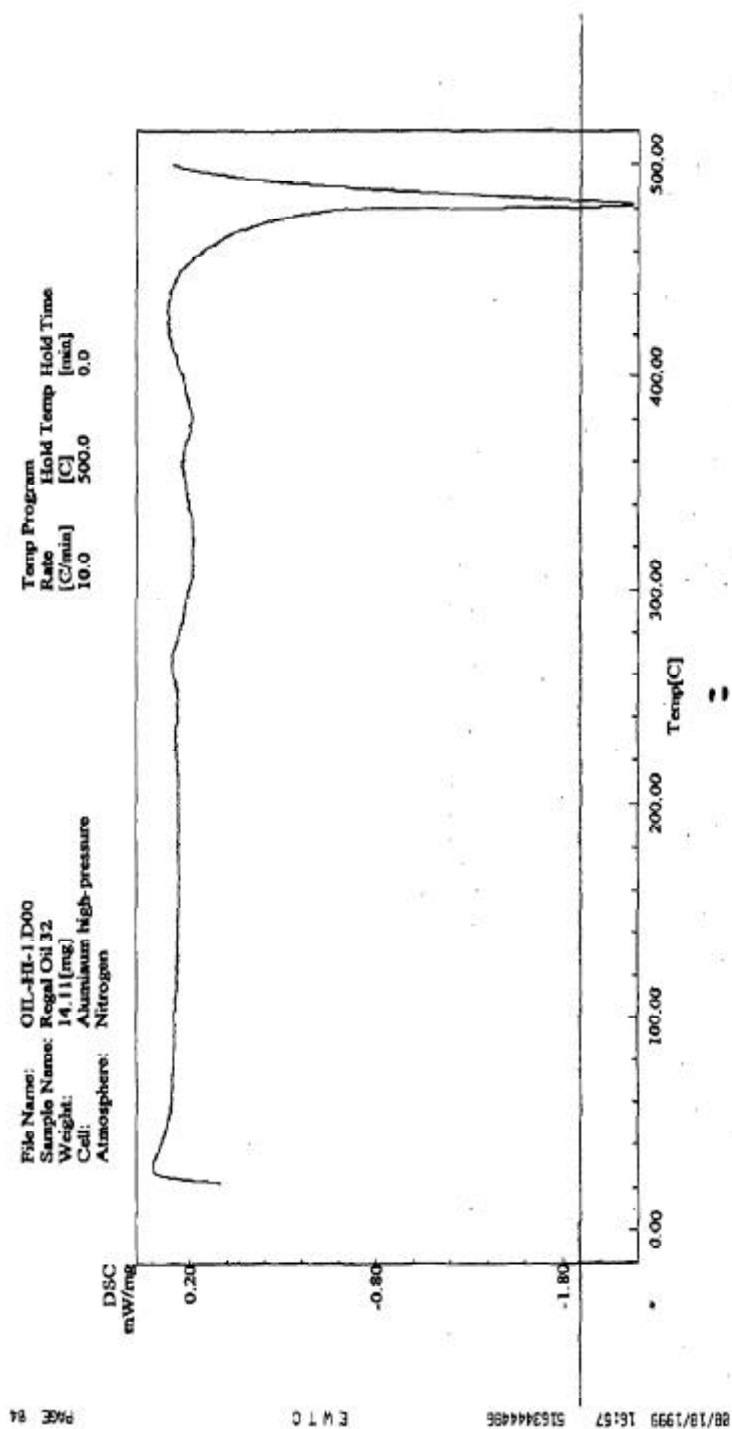


Figure 6. Oil Only in Aluminum Cell.

References

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2. G. A. Beitel, 1999, Analyses of Combustion Scenarios Involving Graphite, Organic Material, Nitrate Salt, and Air During Subsurface Drilling in Pit 9, EDF-ER-060, April.
3. Shaw, P. G., B. Anderson, D. Davis, 1993, Laboratory Scale Vittrification of Low-level Radioactive Nitrate Salts and Soils from the Idaho National Engineering Laboratory, EGG-WTTD-10640, July.